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THE IMPORTANCE OF THE RESIDUAL LAYER IN CHARACTERIZING OZONE EPISODES IN EAST TENNESSEE

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Eric Kevin Hutton

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ABSTRACT

This thesis was written to characterize episodes of high ozone concentrations in East Tennessee. The trajectory analysis of high pressure air masses revealed that the trajectory of a high pressure system impacting East Tennessee was not as important as whether the system stagnated. Four ozone episodes have also been analyzed. In May 1992, stations representative of the residual layer observed an excellent example of a nocturnal increase of ozone due to regional transport that contrasted a simultaneous decrease in ozone concentrations at nearby low altitude monitors. Using ozone isopleth maps and comparisons of individual stations representative of the residual layer and the mixed layer in the three other episodes, it was found that the residual layer can store and transport ozone concentrations of 80-120 parts per billion or greater over large areas. Furthermore, convective mixing the following day can make these concentrations the most important source of ozone for rural areas and small cities similar to Knoxville, where the daily maximums may be within 5-20 parts per billion of the background concentration in the residual layer as measured at White Top Mountain and Mount Mitchell. Thus, this research demonstrates the need for additional studies of vertical concentrations of ozone to determine a community's typical background ozone concentrations and true photo-chemical production rates.

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LIST OF ABBREVIATIONS

AIRS	Areometric Information Retrieval System
AQS	Ambient Air Quality Standard
EPA	United States Environmental Protection Agency
EDT	Eastern Daylight Time
EST	Eastern Standard Time
EZ	Entrainment Zone
ML	Mixed Layer
NOAA	National Oceanic and Atmospheric Administration
RL	Residual Layer
SBL	Nocturnal Stable Boundary Layer
TVA	Tennessee Valley Authority
ppm	parts per million (volume)
ppb	parts per billion (volume)

1.0 INTRODUCTION AND BACKGROUND

The purpose of this research is to determine how the atmospheric residual layer and high pressure systems participate in long range transport of ozone during episodes of high ozone concentrations with emphasis on Knoxville Tennessee and the Southern Appalachians. Vertical profiles of ozone show that nighttime ozone concentrations increase steadily with altitude from the ground surface to the top of the nocturnal stable boundary layer (SBL). Then the concentrations remain constant from the top of the nocturnal inversion to the top of the residual layer (RL). During the following day, these higher concentrations aloft mix down with the air at the ground surface as the mixing height grows from zero to its final height that day [Trainer et al, 1991; Nappo et al, 1989; Broder and Gygax, 1985; Colbeck and Harrison, 1985; Ludwig, 1985; Coffey et al, 1978; Harrison et al, 1978; and Van Dop et al, 1977]. Unfortunately at most low altitude air monitoring stations, the SBL and the daytime vertical mixing create a strong diurnal pattern that very effectively masks both the true vertical nocturnal average ozone concentrations and the importance of vertical mixing to the observed daily maximum ozone concentrations.

However, it has been found in the literature on Whiteface Mountain, New York [Coffey et al, 1978], and Mount Mitchell, North Carolina [Aneja et al, 1989], and in data presented in this thesis from White Top Mountain, Virginia; Dickey Ridge,

Virginia; and Big Meadows, Virginia; and Mount Mitchell, North Carolina that ozone stations on high ridges do not exhibit a strong diurnal pattern equivalent to those observed at nearby lower altitude stations. Instead, this thesis shows four examples of high altitude concentrations exhibiting a multi-day cycle for the rise and fall of ozone concentrations. Furthermore as presented in this thesis, the comparisons of ozone monitoring stations on ridges exposed to the RL, called residual layer monitors (RL stations), and nearby ground level ozone stations, called stable boundary layer monitors (SBL stations), show that the midday SBL station concentrations are within 5 parts per billion (ppb) of simultaneous eleven hour dampened RL concentrations as far away as 20 miles and within 20 ppb if the stations are less than a few hundred miles distant. Furthermore, results from ozone isopleth maps show large areas of hundreds of square miles with daily maximum ozone concentrations greater than 80 ppb. Ozone concentrations in the following night's residual layer would be expected to have similar concentrations patterns. Also the results of this thesis show that large differences in ozone concentrations observed between monitoring stations appear to be the result of contrasting meteorology between the stations.

Together, these results and the analysis of high pressure trajectories impacting Knoxville presented in this thesis, show that high pressure systems and the RL combine to concentrate, store, and spread ozone and its precursors over

large distances and land areas of several hundred square miles. Compared to the edges of the anti-cyclone, the subsidence near the center of the high pressure system concentrates ozone concentrations by compressing the mixing height, or mixing layer, increasing the temperature, and increasing biogenic and anthropogenic emissions [Trainer et al, 1991; Cardelino and Chameides, 1990; Stull, 1988; and Wark and Warner, 1981]. Furthermore, the center of the high pressure system has clear skies which lead to the formation of the RL [Stull, 1988], and thus to nocturnal ozone storage. As the slug of air represented by the high pressure system moves across the United States, these concentrated emissions should be expected to move with the anti-cyclone [Colbeck and Harrison, 1985, and Wight et al, 1978]. Therefore, in areas of the United States away from the largest metropolitan areas, the most important factors leading to high ozone concentrations on a particular day are the high pressure system's stagnation and the subsequent distribution of ozone in the RL.

The data presented in this thesis shows that during the July 9, 1988, episode, ozone concentrations in Knox County, Tennessee reached 150 ppb and concentrations in the RL as measured at White Top Mountain were as much as 115 ppb on that same day. Other observations at White Top, Mount Mitchell, and Dickey Ridge exceeded the United States Environmental Protection Agency's (EPA) Ambient Air Quality Standard (AQS)

for ozone of 0.12 parts per million. Thus, the RL plays an exceedingly important role in the observations recorded at ground level monitoring stations. However, it has not been determined where this RL ozone has originated. Even so, estimating the amount of ozone transported into an area is an important part of any ozone abatement strategy because it defines a baseline concentration over which the local air pollution agency has no control. Thus, more research is needed to determine if these high RL concentrations are the result of local production in the vicinity of the monitor accumulating over several days, regional transport from larger metropolitan areas, or the accumulation of pollution from the many square miles of surface area that the air mass has traveled before reaching the monitor.

2.0 LITERATURE REVIEW

In studies of air pollution, the most important part of the atmosphere is the boundary layer because nearly all anthropogenic and biogenic emissions are emitted and trapped there. Stull [1988] defines "the boundary layer as that part of the troposphere that is directly influenced by the presence of the earth's surface, and responds to surface forcings with a timescale of about an hour or less." As shown in figure 2-1 for sunny days typical of high pressure systems, the boundary layer is further divided into the mixed layer, ML; the nocturnal stable boundary layer or nocturnal inversion, SBL; the residual layer, RL; and the entrainment zone, EZ. The force of gravity, the ideal gas law, and solar radiation play vital roles in creating vertical temperature profiles that create the stability conditions which generally describe these sublayers and characterizes the amount and type of pollution in these layers. Furthermore, an understanding of how these layers interact with themselves and high pressure systems is vitally important to understanding many of the episodes of high ozone concentrations in East Tennessee.

2.1 Atmospheric Stability Conditions

Gravity acts to hold the atmosphere on the Earth's surface. The mass of atmosphere above a certain point is proportional to the atmospheric pressure on that point.

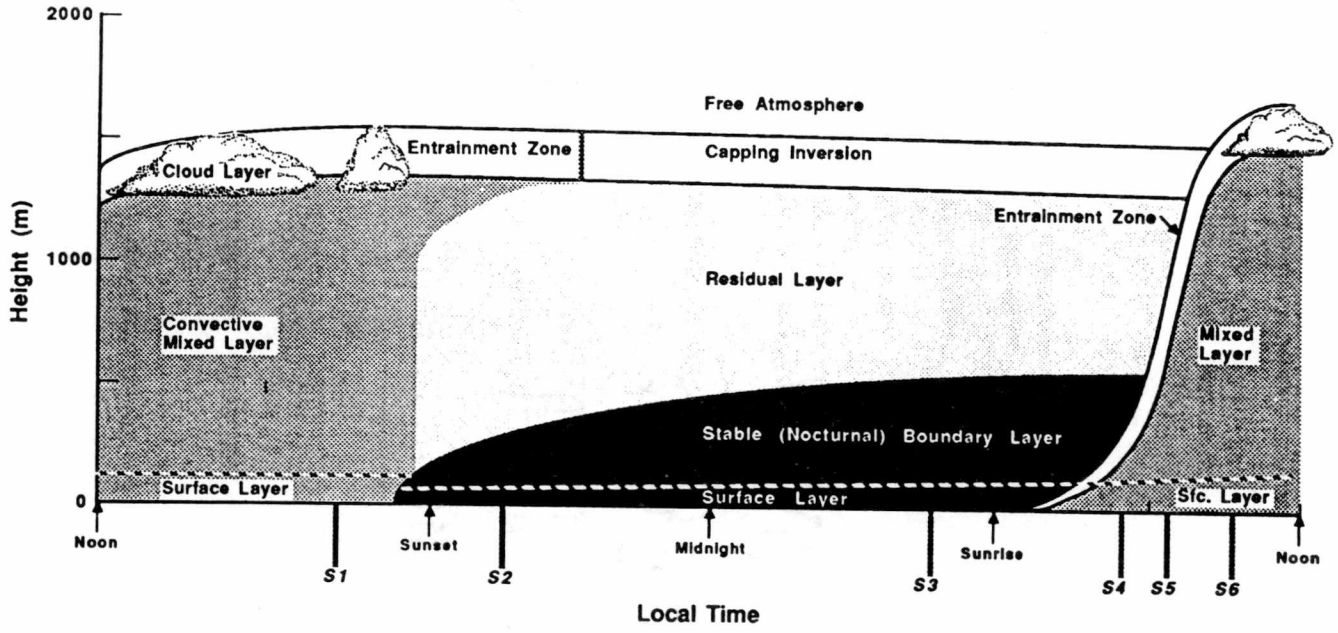


Figure 2-1. Boundary Layer Structure in High Pressure Systems

Source: Stull, R. B. An Introduction to Boundary layer Meteorology. London: Kluwer Academic Publishers. 1988.

Consequently, pressure on a parcel of air decreases as it ascends through the atmosphere. Considering that the parcel has a known mass, volume, and gas constant, then by the well known ideal gas law, temperature will also decrease [Stull, 1988]. The theoretical temperature decrease, which occurs as a function of increased altitude with no net heat exchange is called the *adiabatic lapse rate.* A parcel's water content is the largest variable that normally affects the lapse rate, which for dry air is 9.8°C/km [Wark and Warner, 1981]. In order to account more clearly for varying moisture contents and pressure values with altitude, meteorologist have derived the virtual potential temperature, $\overline{\theta}_v$, which translates the ambient adiabatic lapse rate from a line with negative slope to a vertical line.

Since the atmosphere can have many different temperature profiles that vary from the adiabatic lapse rate, the atmosphere can have varying degrees of stability. For example, if the ambient atmosphere is cooling faster than its theoretical adiabatic lapse rate as elevation increases, then the atmosphere is referred to as *superadiabatic, well mixed,* or *unstable;* an air parcel rising in altitude will tend to follow the adiabatic lapse rate, become warmer than the surrounding air, and therefore will continue to rise. Similarly if the parcel descends it will become colder than its surroundings and gravity will continue to pull it to the

ground. On the other hand, if the atmospheric lapse rate is less than the adiabatic lapse rate, then the atmosphere is referred to as *subadiabatic* or *stable*. This situation is also called a *temperature inversion*. If a parcel of air rises, gravity pulls the parcel back down because it is colder than its surroundings; while a decrease in altitude will cause the parcel to become warmer than its surroundings, causing it to float back up.

However, as figure 2-2 demonstrates using virtual potential temperature, $\overline{\theta}_v$, the local temperature profile does not provide enough information to determine stability; one must also consider an air parcel's buoyancy and ability to sink through warmer air. The dashed lines in the figure help demonstrate this point by showing potential air parcel movement. Essentially, once a parcel begins to move vertically due to local instability and a local disturbance, it will continue to move until it reaches air with the same $\overline{\theta}_v$. For example, consider a local unstable region at the ground surface just below an area of neutral stability like that shown figure 2-2-f. Instead of just the small superadiabatic portion at the ground surface being unstable, the entire domain of neutral stability is also unstable. The cool air aloft will displace the warm air at the ground, which will rise until it reaches air above the neutral stability

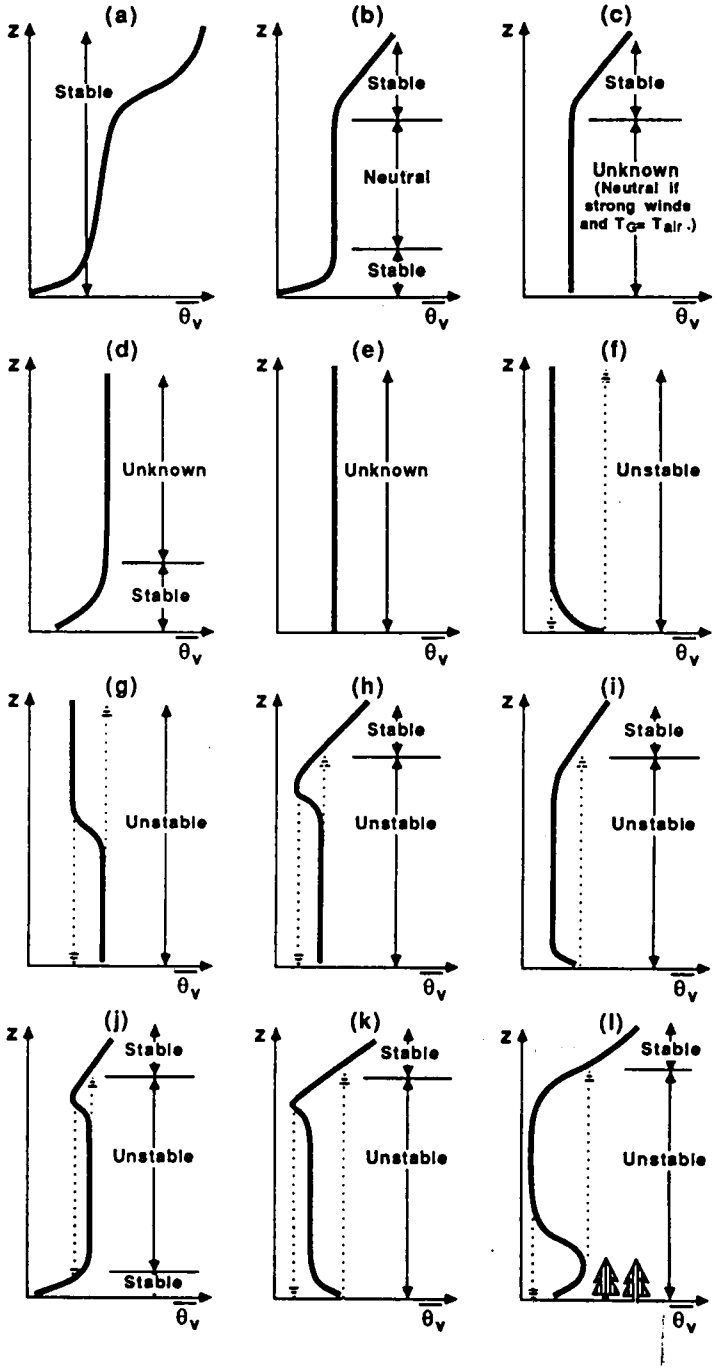


Figure 2-2. Static Stability as a Function of the Virtual Temperature Profile. Dotted Lines Denote Parcel Movement.

Source: Stull, R. B. An Introduction to Boundary Layer Meteorology. London: Kluwer Academic Publishers. 1988

with the same $\overline{\theta}_v$. In turn the rise of the warm air will displace more cold air and begin the cycle again.

2.2 Characteristic Vertical Temperature Profiles of the Nocturnal Stable Boundary Layer, Residual Layer, and Mixed Layer

Figure 2-3 shows 6 typical mean $\overline{\theta}_v$ profiles for the boundary layer. The marks S1-S6 in figure 2-3 correspond to the marks S1-S6 in figure 2-1 and are used to demonstrate how the temperature profiles change as the boundary layer evolves in a 24 hour cycle.

As the sun sets on a clear calm night, the source of heating is no longer present and the temperature profile begins to look like S2. Without solar radiation the earth and the lowest portions of the boundary layer cool rapidly through radiative cooling. Although this heat loss occurs throughout

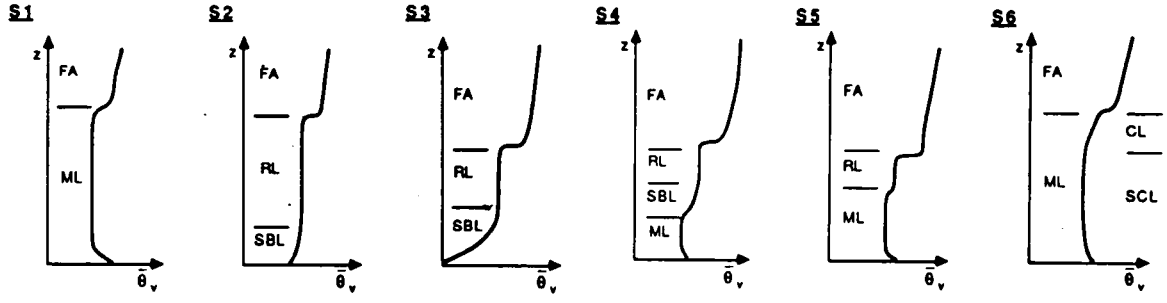


Figure 2-3. Typical Temperature Profiles Associated with Boundary Layer Evolution.

Source: Stull, R. B. An Introduction to Boundary Layer Meteorology. London: Kluwer Academic Publishers. 1988

the night at all altitudes, the amount of heat lost by a volume of air over any time period during the night is generally inversely proportional to the parcel's elevation from the ground surface. This pattern of heat loss is strong enough to form a temperature inversion a few meters thick at the ground surface within an hour of sunset. As successive layers aloft adjacent to the ground inversion lose more heat, they too become part of this inversion known as the *nocturnal stable boundary layer* (SBL) or, less precisely, the *nocturnal inversion*. By morning this nighttime layer may be 1000 m from the ground surface to its top. However, 100 m to 500 m is a more typical depth. Points S2 and S3 demonstrate this loss of heat at the ground surface over time and the resulting increase in the SBL height.

Between the SBL and the previous days entrainment zone is the residual layer or RL. Air from this layer will not sink into the SBL because it is not cold or dense enough. However, gravity will pull the colder air toward the SBL and create a temperature profile that is very near the adiabatic lapse rate.

Typically when the sun rises on the following day there will be no clouds and a strong superadiabatic lapse rate will form near the ground surface capped by an inversion. The layer between the ground surface and the inversion is the daytime mixed layer or ML. The bottom of the inversion is called the entrainment zone or EZ. At first the sun only

warms a very short section of the atmosphere a few feet or meters high. The warm air is buoyant because gravity pulls colder air aloft from the bottom of the EZ to the ground and displaces the warm air. However, the heat reflected from the earth is more than enough to warm this descending cold air to at least the temperature of the air it replaced. Consequently, the process becomes cyclic, increases the temperatures below the EZ, and, thereby, erodes the bottom of the capping inversion. The growth of the ML has an exponential shape until it slows down some time after mid day and reaches typical heights of 3000 to 6000 feet, or even 15000 feet over some deserts. Point S1 is the temperature profile for the previous day's ML before the SBL formed, while points S4-S6 show the growth of the ML through the SBL and RL.

2.3 The Effects of the Nocturnal Stable Boundary Layer, Residual Layer, and Mixed Layer on Pollution Plumes.

A well developed SBL requires clear skies and calm winds. In such a situation, gravity keeps the coldest and densest air at the ground surface and insures that there is a strong temperature inversion at the ground surface that gradually blends into the neutrally stable RL. The amount of vertical mixing in these nocturnal layers then increases with altitude as stability decreases. Thus as shown in figure 2-4, the higher the altitude of the pollution source the more the plume

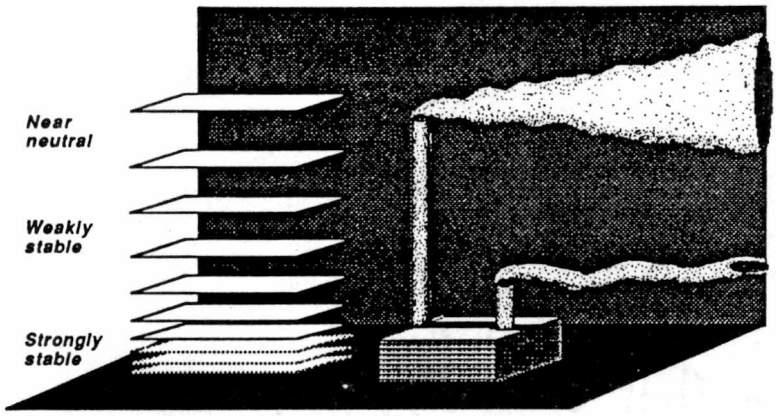


Figure 2-4. The Effects of Decreasing Stability on Point Source Plumes.

Source: Stull, R. B. An Introduction to Boundary Layer Meteorology. London: Kluwer Academic Publishers. 1988

disperses vertically. In the SBL the plume barely expands vertically but may expand considerably in the horizontal. However, in the neutral stability of the RL, the plume will expand equally in both the horizontal and vertical directions. In the figure the space between the horizontal planes drawn on the left side of the smokestacks is proportional to the amount of vertical mixing in the atmosphere and inversely proportional to the degree of stability in the atmosphere.

One of the most important aspects of the SBL is that it prevents air in the RL from dispersing into it. As an example, figure 2-5 shows a point source plume that originates low in the RL just above a strong SBL. Assuming that the plume will spread like a cone from the stack, then the SBL would seem to rise high enough as the night progresses for the

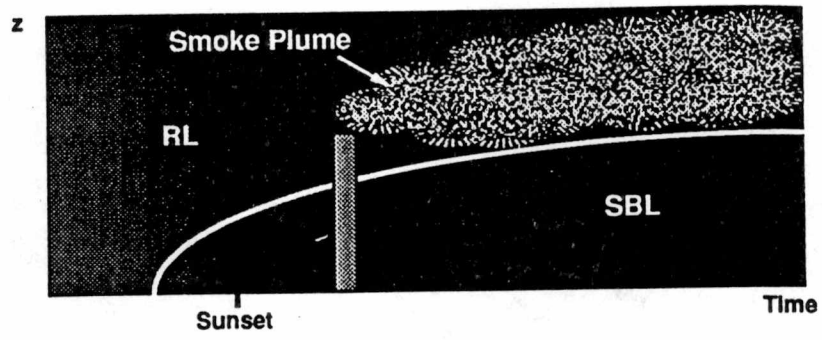


Figure 2-5. Lofting of a Smoke Plume by the Stable Boundary Layer.

Source: Stull, R. B. An Introduction to Boundary Layer Meteorology. London: Kluwer Academic Publishers. 1988

bottom of the plume to filter into the stable layer. However, in process referred to as *lofting*, the temperature inversion reflects the lowest portion of the plume back into the RL. Consequently, the plume and other components of the RL are trapped in that layer and will not interact with any ground surfaces at lower altitudes. Thus, although the RL initially has the temperature, chemical and wind profiles of the ML from which it evolves, it develops neutral stability and can undergo only limited chemical changes as the night progresses.

Usually the importance of the RL to air pollution is first noted some time after sunrise when daytime mixing begins. The process starts within an hour after sunrise. During a typical sunny day under the influence of a high pressure system, the sun and ground quickly heat a layer of

air at the ground surface, reversing the temperature inversion and creating a small well mixed zone a few meters thick. While the ML is still short, it is simply a remixed version of the SBL; and probably has only low concentrations of pollution. However, it grows by entraining the air just above it and this mixing process is thorough enough to quickly homogenize the air just entrained throughout the entire layer [Stull, 1988]. Thus, as shown in figure 2-6, when it grows vertically to reach plumes in the SBL or RL, it mixes them into the RL in a process called *fumigation* [Stull, 1988; Wark and Warner, 1981]. Since the RL undergoes only limited chemical changes, then its ozone concentrations at the time it dissipates should be similar to the concentrations to the ML from which it evolved. Thus, concentrations of ozone in excess of 80 ppb produced one day over a metropolitan area may

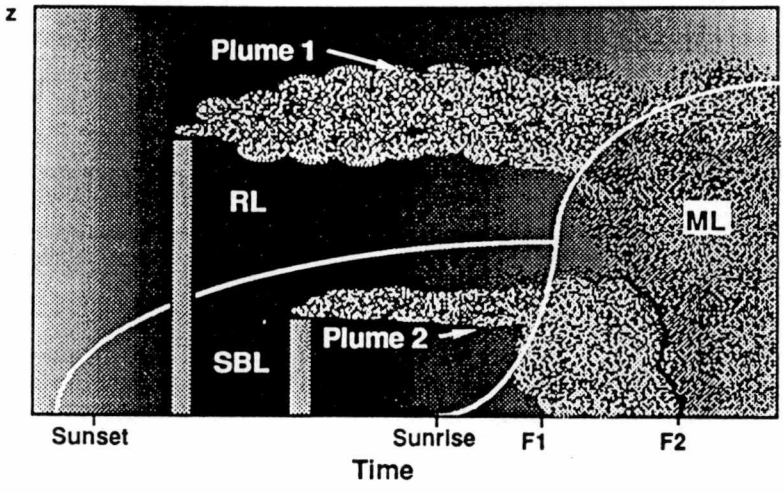


Figure 2-6. Plume Fumigation as a Source of Pollution in the Mixed Layer.

Source: Stull, R. B. An Introduction to Boundary Layer Meteorology. London: Kluwer Academic Publishers. 1988

move in the RL to be spread the next day into the ML at another location. Thus, the RL has the potential to store and transport large quantities of ozone as a background source for many medium sized cities and rural areas [Stull, 1988].

2.4 Contrasting Rural and Urban NO_x Concentrations

The importance of NO_x concentrations for ozone concentrations are illustrated by the equations below

$$NO_2 + h\nu \rightarrow NO + O \quad (1)$$

$$O + O_2 \rightarrow O_3 \quad (2)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (3)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (4)$$

These equations would lead to an equilibrium of NO, NO_2, and ozone if not for the presence of hydrocarbons that react with NO to create NO_2 and thereby prevent it from reducing the ozone concentrations by reaction 3. The reaction rate of equation 4 is very slow in comparison to the other three equations and is not expected to be of primary importance during the day . One result of these well known equations in the absence of additional hydrocarbon emissions or sunlight is the depletion of ozone as equations 3 and 4 dominate the cycle [Trainer et al, 1991; Leahey and Hansen, 1990; Broder and Gygax, 1985; Wark and Warner, 1981; and Harrison et al, 1978].

It has been observed in extensive urban areas that late afternoon or early evening NO_x concentrations are often higher than the concurrent ozone concentrations. These higher concentrations are the result of heavy automobile traffic during the evening rush hour and can deplete ozone faster than the solar radiation can replenish it. Thus, it has been shown that in these areas NO_x concentrations scavenge ozone and account for its decrease to near 0 ppb at night [Wark and Warner, 1981]. Although urban areas and plume sources often have more than 20 ppb NO_x, table 2-1 shows that measurements in truly rural areas often have less than 5-10 ppb of NO_x. In fact many rural areas have only around 1 ppb of NO_x. Furthermore, there is some evidence that NO_x concentrations may decrease with height [McKeen et al, 1991; Trainer et al, 1991; and Broder and Gygax, 1985]. Thus, in many rural areas NO_x, concentrations and equations 3 and 4 above cannot account for a substantial decrease in even the estimated natural background concentration of ozone of 10 - 20 ppb [Altshuller, 1987; Broder and Gygax, 1985; and Harrison et al 1978].

2.5 Ground Level Nocturnal Ozone Depletion--NO_x Scavenging or Dry Deposition?

Even though rural NO_x concentrations are too low to scavenge much ozone, most rural areas also experience a strong nocturnal drop in ozone concentrations [McKeen et al,

Table 2-1. Typical NO_x Concentrations

Year	Concentration of NO_x (ppb)	Location	Situation or Source	Author
1990	greater than 10	Calgary	Two stations north of Calgary	Leahey, Hansen
1987	20-40	Meteorological mast 25 km north of Denver and 20 km east of Boulder. Height limit is 300 m.	NO_2 at edge of power plant plume	Van Valin, Ganor
	50		NO at center of power plant plume	
	20-30		NO_2 in urban plume	
	5-10		Daytime pollution episode without a specific origin	
1985	35	Reuss Valley, Switzerland	Below Ridge Crest	Broder and Gygax
	5		Above Ridge Crest	
1985-1987	200	Los Angeles, 1985-1987, Average, Monday-Friday	NO Monitor Survey	Hogan et al
	90		NO_2 Monitor Survey	
1978	5	Heysham England	1.5 km from the nearest habitation	Harrison et al
1987	5-10	Rural areas within heavily populated portions of Europe and the United States	Literature Survey	Altshuller
1964	1.0	Unpolluted areas of the United States	Literature Survey	Wark and Warner
	80	Urban metropolitan areas of the United States	Literature Survey	
	250	Los Angeles, London, and Japanese Cities	Literature Survey	
1991	less than 2.4	Most of Eastern United States	Model Output, 1500 EST	McKeen
	greater than 9.6	Select areas of Eastern United States, mostly urban	Model Output, 1500 EST	
1990	96	Atlanta	Input for base case model	Cardelino, Chameides

1991; Trainer et al, 1991; Broder and Gygax, 1985; and Harrison et al, 1978]. To find the reason for the strong nocturnal drop in rural ozone concentrations Harrison et al [1978] examined atmospheric stability conditions and NO_x and ozone concentrations at a rural site near Heysham, England, but still "1.5 km from the nearest habitation or roads, within a sparsely populated area." Only equations 3 and 4 above and those of a few highly reactive alkenes are fast enough to be able to account for the fast rural nocturnal depletion of ozone they observed. By these reactions each molecule of NO can cause the loss of up to two O_3 molecules. However, they measured less than 1 ppb of NO and less than 4 ppb of NO_2. Furthermore, the concentration of total alkenes is not as high as NO_x. Since rural areas will not replenish the NO_x or alkene concentrations, these reactions alone cannot account for the 50 ppb drop in ozone at their site. Thus, atmospheric chemistry alone does not account for the loss of ozone at night.

They also propose and reject the idea that ozone depletion might occur if ozone reacted with chemicals already present in the atmosphere when the nocturnal inversion formed. The ML has uniform ozone concentrations throughout its height just before the nocturnal inversion forms. Since the SBL dramatically slows vertical mixing, then the ozone concentration should be uniform if the depletion is caused by chemical reactions. However, the actual ozone profiles

observed in their study showed a steady increase in ozone aloft with increasing height in the inversion [Harrison et al, 1978]. These profiles are similar to ozone profiles in articles by Ludwig, 1985; Coffey et al, 1978; Van Dop et al, 1977; Van Valin and Ganor, 1987; and Broder and Gygax, 1985. After exhausting these possibilities, they turned to surface deposition.

They cited an article by Garland and Penkett that stated that the destruction of ozone in a well developed ML of a specific height is a first order reaction with a rate constant which is equal to the deposition velocity. Using a deposition velocity of 1 cm/s, they calculate that it would take 110 min for the concentration to drop from 75 to 20 ppb for a layer 50 m in height. Since it actually took 4 hours to achieve this reduction at their station, it would appear that this rate is too fast. However in comparison to the ML, the strong stability of the SBL dramatically slows vertical mixing, thereby lengthening the time it takes for ozone at the height of the monitor's intake to deposit to the ground and also decreasing the deposition velocity. However, the stability also increases the time it takes ozone in the RL to replenish the ozone lost at the monitor altitude. Consequently, the stronger the nocturnal inversion is the stronger the gradient of ozone concentrations from the ground to the RL and the faster the ozone concentrations at the ground surface approach 0 ppb [Harrison et al, 1978].

Nevertheless, if Harrison et al [1978] had used a deposition velocity around 0.5 cm/s they could account directly for their more slow decrease in ozone. Such a velocity would not be unreasonable since Lenshow et al [1981] calculated a daytime value of 0.47 cm/s over rangeland and irrigated farmland near Denver, Colorado. As just explained, the nocturnal deposition velocity should be even slower than the daytime. The vertical ozone concentrations in this study ranged from 29 ppb to 45 ppb at altitudes from 0 to 1.5 km above the ground surface from 9:49 to 11:46 local standard time on September 19, 1979 [Lenschow et al, 1981]. Van Dop et al [1977] cite that deposition velocities range from .1 to 2 cm/s. For decreases in ozone that take from 4-8 hours at a mast near Cabauw, the Netherlands, they calculated a deposition velocity of 0.13 cm/s [Van Dop et al, 1977]. Thus, as summarized in table 2-2 , there are ozone deposition rates in the literature that are slow enough to account for the observed ozone depletion in the study by Harrison et al [1978].

In a similar study in the Swiss Alps on terrain induced effects on ozone and other parameters, Broder and Gygax [1985] have also worked directly with the ground deposition of ozone. In previous research they found that "homogeneous chemistry accounts on average for 19% (extreme values were 4% and 54%) of the observed destruction rates. The main effect is due to the reaction between [nitrogen oxides] and ozone. The

Table 2-2. Typical Ozone Deposition Velocities

Deposition Velocity cm/s	Author	Location	Ground Surface
0.47	Lenschow et al	Denver	Rangeland and irrigated fields
1.0	Harrison et al	Heysham England	Rural, estimated
0.13	Van Dop et al	Caubaw, The Netherlands	Rural
0.1-2.0	Van Dop et al	Citation in their article	

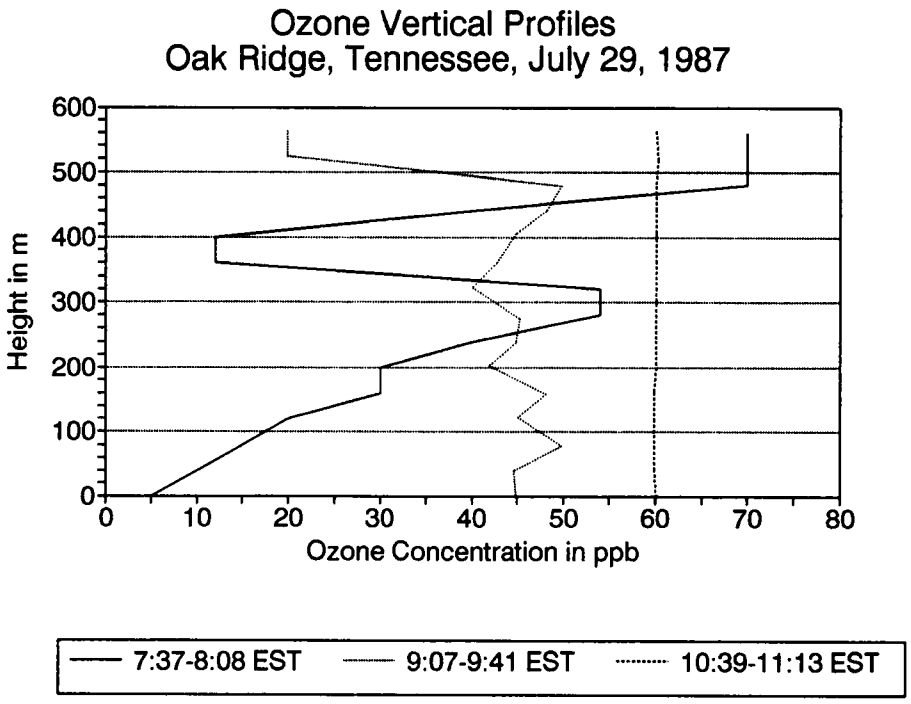
remaining ozone destruction is attributable to the dry deposition of ozone at the surface." In this particular study of the Reuss Valley, they noted that air centered over the valley and below the ridge tops showed a decrease in ozone concentration, an increase in water vapor, and a decrease in temperature. The decrease in ozone was greater than that attributable to chemical reactions. The increase in water vapor had no atmospheric or water body source, and there also appeared to be no sink for the temperature loss. However, by accounting for drainage flows with a return flow to the air above the ridges centered over the valley center, they concluded that the air deposited ozone to the surface, absorbed water from evapo-transpiration, and lost heat to the ground as it moved down the slope. They then observed these effects in the air above the ground in the Reuss valley. They

go on to conclude that as a large air mass travels over many such valleys, these individual circulations will have an additive effect on the air masses ozone concentration, humidity, and temperature [Broder and Gygax, 1985]. Thus, surface deposition in the nocturnal inversion is largely responsible for the nightly decrease in ozone concentrations at rural sites.

2.6 Some Examples of the Effects of the Stability in the Boundary Layer.

The stronger the atmospheric stability the less a point source or urban plume is expected to disperse into the atmosphere. Furthermore, during the existence of a strong SBL, the RL is cut off from ground influences and may yield very different observations from the SBL. The study by Van Valin and Ganor [1987] on pollution concentrations in plumes depends on these assumption as many of their plumes were detected at night under the influence of the SBL.

For another example consider figure 2-7 which is data from near Knoxville in Oak Ridge, Tennessee, on July 29, 1987 reported by Nappo et al [1989]. At three different times a tethered balloon was released to take ozone, temperature, and moisture measurements during the ascent. The 7:37-8:08 Eastern Standard Time (EST) measurements showed a strong temperature inversion coupled with a strong decrease in ozone concentrations from 70 ppb at 500 m above ground to 5 ppb at



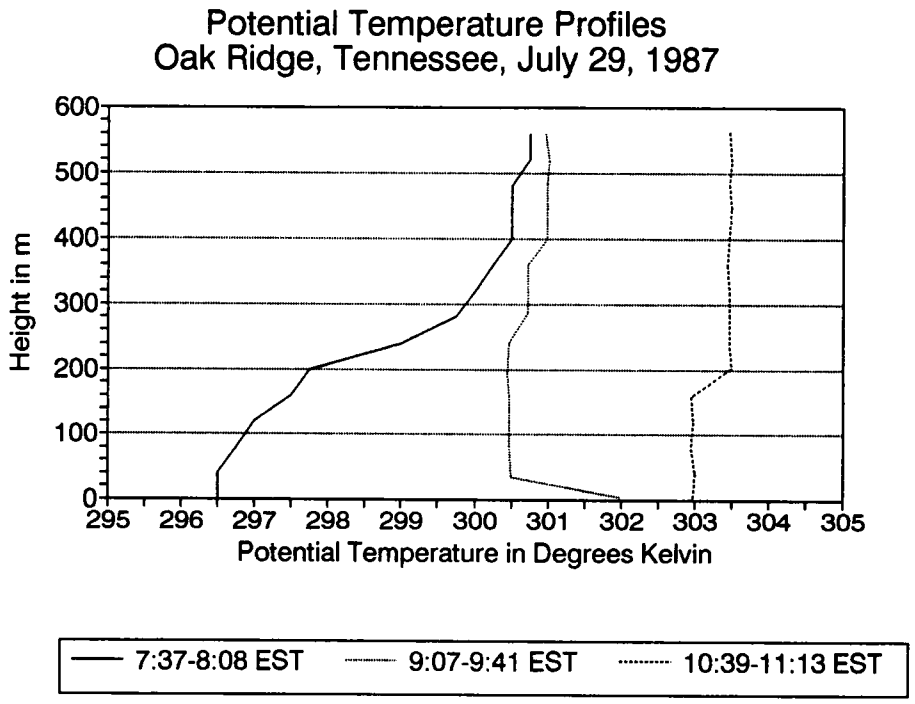


Figure 2-7. Ozone and Potential Temperature Profiles, July 29, 1987.

Source: Nappo, C. J.; Herwehe, J. A.; Thompson, A. M.; Observations of Ozone Profiles in the Developing Convective Boundary Layer. Ozone in the Atmosphere. Bojkov, R. D.; Fablan, P Eds., Deepak Publishing. p. 477-480. 1989.

ground level. Above 500 meters the temperature and ozone concentrations became constant and would seem to indicate the possible top of the SBL. However, without further vertical information there can is no conclusive proof that this assumption is true. One of the intriguing parts of this profile is the strong drop in ozone concentrations between 320 and 480 m above ground. This is reported to be the result of a high NO_x plume that has depleted ozone and that comes from the nearby coal fired steam plant, Bull Run [Nappo et al, 1989]. However, applying research conducted by Van Valin and Ganor [1987] on plumes impacting a meteorological mast near Boulder Colorado, a graph of NO_x content would show an equally strong peak at these altitudes [Van Valin and Ganor, 1987]. By the 9:07-9:41 ascent the temperature inversion had reversed and had become quite unstable in the first 20 m above the ground [Nappo et al, 1989]. Applying the stability principles discussed earlier, then the buoyancy of the air at the ground surface will make the actual height of the instability the entire vertical slice measured in the present example [Stull, 1988]. Thus, as Nappo et al [1989] suggest, the strong superadiabatic lapse rate had caused the ozone to become mixed up until at least the 500 m height by 9:41 EST [Nappo et al, 1989]. The author of this thesis speculates that the drop in ozone concentrations at this point may be due to a rise in the plume from Bull Run Steam Plant. Certainly by the 10:39-11:13 ascent ozone concentrations had become well mixed throughout

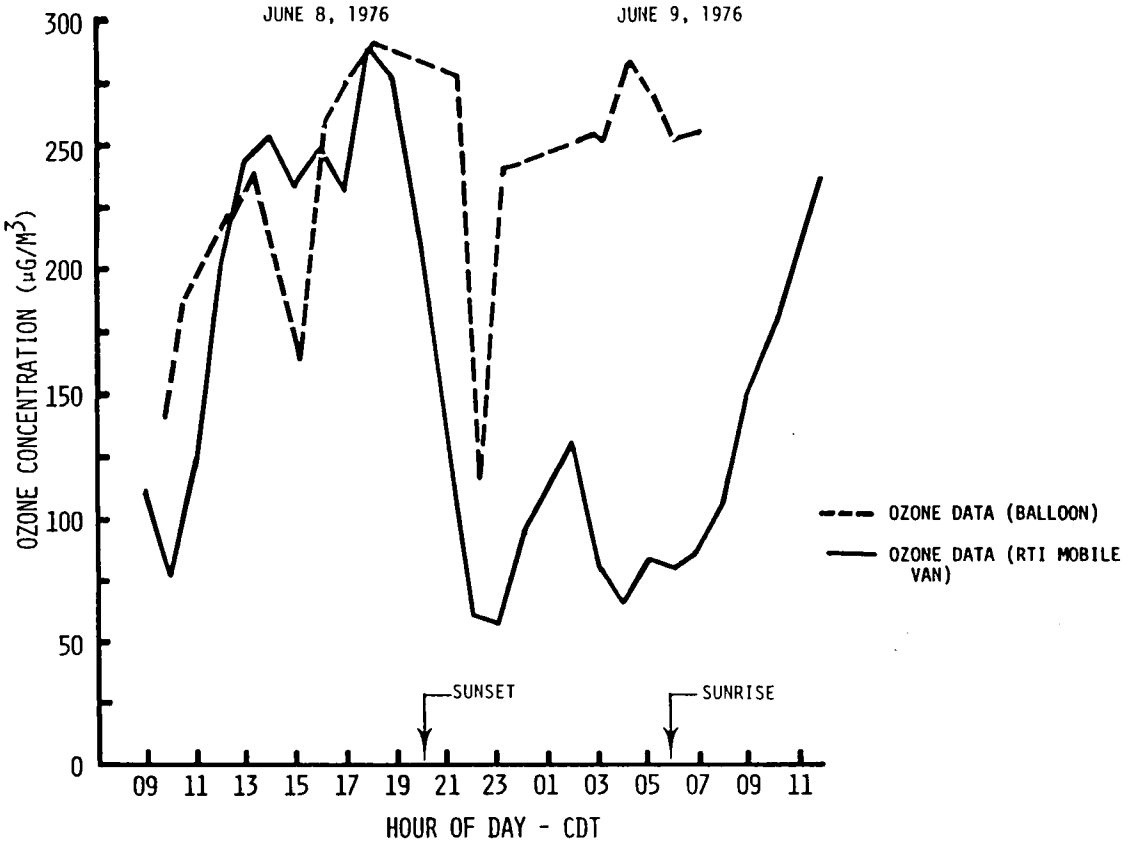


Figure 2-8. Ozone Concentrations Traveling from Saint Louis to Southwestern Indiana at the Ground and about 800 m above Ground.

Source: Decker, C. E.; Worth, J. J. B.; Ripperton, L. A.; and Back, W. D., Ambient Monitoring Aloft of Ozone and Precursors Near and Downwind of Saint Louis. USEPA-450/3-77-009. 1977.

the depth considered as the temperature continued to rise [Nappo et al, 1989].

Clearly, this example shows that during the existence of a SBL, ozone concentrations aloft can be much higher than near the ground. It also demonstrates that the stability of the SBL prevents vertical mixing as evidenced by the intact plume from the steam plant. There was also the evolution of a strong SBL into a ML with a concurrent entrainment and mixing of ozone concentrations aloft into the ML, which raises concentrations near the ground and lowers concentrations aloft. It can probably be assumed that the increase in ozone concentrations from 9:41 to 11:13 was the result of mixing more ozone from aloft. This point arises from the fact that initially ozone concentrations are expected to be constant in the RL and that at 500 m the 8:08 ozone concentrations was the highest on the graph [Nappo et al, 1989].

Another intensive study occurred near Saint Louis. A hot air balloon was launched at 8:57 Central Daylight Time, June 8, 1976, from Arrowhead Airport near Saint Louis with the Gondola. Suspended 61.5 m below the gondola was equipment to measure ozone and other atmospheric measurements. Staying in near proximity to the balloon was a specialized van also with the capability to measure ozone concentrations. Generally, the balloon maintained a flight altitude of 800 m. As shown in figure 2-8, nocturnal ozone concentrations in the RL near

the balloon ranged from 230 (115 ppb) to 290 micrograms/cubic meter (145 ppb), while near the van in the SBL concentrations ranged from 50 to 125 micrograms/cubic meter (25-62 ppb). The one exception occurred between 21:41 and 23:10, June 8. At that time the flight crew noticed a pungent hydrocarbon odor and the 22:00 hour grab sample showed a very strong increase in Non-methane-hydrocarbons. "The location of the balloon at 22[:]19 was 30 km downwind of a refining and 50 km downwind of a power plant." The researchers also indicated that winds in the SBL and RL came from different directions. [Decker et al, 1977].

Thus, the Saint Louis example shows that ozone concentrations aloft can be much higher than those at the ground surface. The authors of the paper suggest that the high ozone concentrations (greater than 100) observed in Southwestern Indiana are the result of transport from Saint Louis. Certainly this seems plausible since the balloon traveled from west of Saint Louis to Southwestern Indiana. However, no comparison of actual wind speed and balloon speed is given in the article. Thus, there is no determination of how efficient the wind was at pushing the balloon or of how much faster the air may have traveled than the balloon. Thus, it appears reasonable to the author of this thesis, that the real extent and impact of the urban plume could have been much further and widespread.

Other important facets of the Saint Louis experiment include the hydrocarbon plume and windshear. Just as the stability near Oak Ridge prevented the Bull Run plume from dispersing, the neutral stability of the RL allowed an anthropogenic plume to travel some distance without dispersing and mixing into the general atmosphere. Furthermore, the wind shear provides a demonstration of the SBL isolating the RL from ground level influences, especially on wind direction and speed. One of the points already discussed concerning the articles by Nappo [1989] and by Van Valin and Ganor [1987] is the existence of well defined plumes with high NO_x concentrations and low ozone concentrations. Also as mentioned the Saint Louis experiment seems to have passed through a well defined plume from a refinery [Decker et al, 1977].

Furthermore, Trainer et al [1991] found a lofted plume in their data at Scotia Pennsylvania that affected their modeling. They noticed a strong daily increase in NO_x concentrations that appeared to be similar to the increase found in larger cities due to the morning rush hour. However, since there were not enough such sources near their station they concluded that a high NO_x plume had been trapped in the SBL or RL above them. When the ML grew to include that elevation, the NO_x in the plume was entrained into the ML and caused the ground level concentrations to rise. As the ML continued to grow, it diluted the NO_x content at the ground by

mixing in relatively clean air from above the plume [Trainer et al, 1991].

Ludwig [1985] also examined a peculiar event in which a low pressure trough caused a night-time maximum as it passed several consecutive ozone monitoring stations. An analysis of the wind speed and directions showed that air from New York City would not have reached these stations at the same time as the night time maximums. He concluded that the nocturnal inversion separated ground level air from the relatively ozone rich air aloft. The trough then caused these maximums as it mixed these two isolated layers together. He also noted that the air aloft was free to move long distances without interference as long as it remained above the inversion [Ludwig, 1985].

Coffey et al [1978] also examined data from Whiteface Mountain in upstate New York and 100 km south of there in Pack Forest, which is presented in figure 2-9. Both stations have no direct anthropogenic influences. At 1519 m elevation Whiteface Mountain is normally in the RL well above the SBL and observes no diurnal ozone cycle; while Pack Forest is in a valley, lies below the nocturnal inversion, and observes a diurnal cycle due to ground deposition and vertical mixing. Interestingly, the daily maximum at Pack Forest very often rises to within a few parts per billion of the concurrent concentration at White Face. Thus, it is apparent that ozone concentrations in low altitude rural areas is depleted at

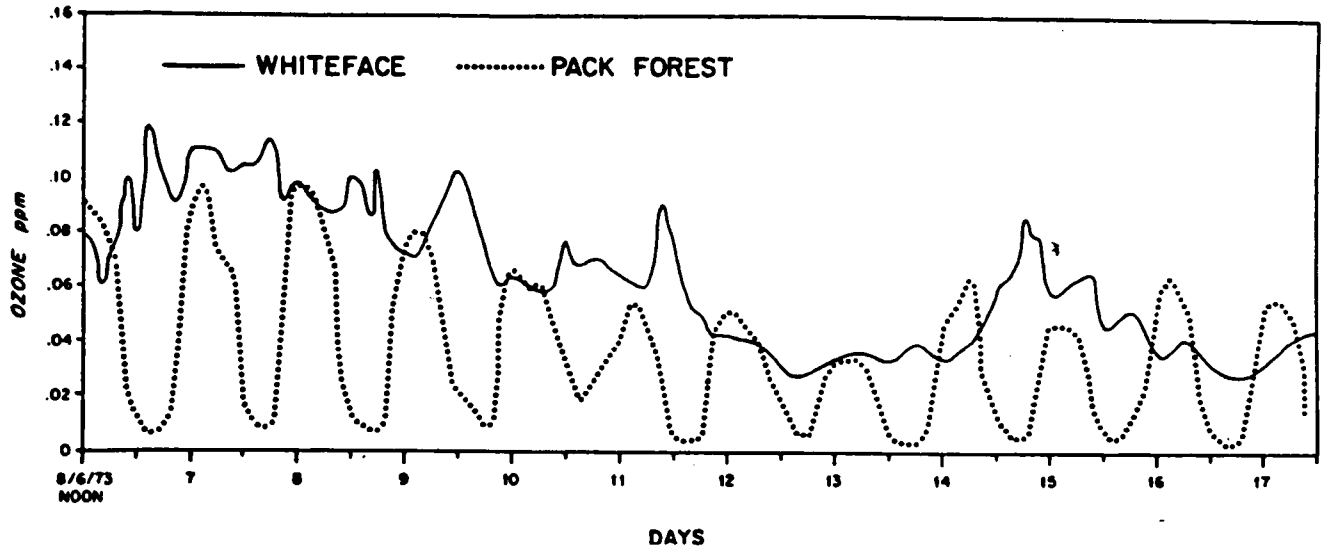


FIG. 8—*Ozone concentrations at Whiteface and Pack Forest, 6-17 Aug. 1973.*

Figure 2-9. A Comparison of Ozone Concentrations on Whiteface Mountain and in Pack Forest.

Source: Coffey, P.E., Whitby, R.A., Stasiuk, W. N., Husain, Liaquat, and Mohnen, V. A., "Ozone Measurements at Several Rural and Urban Sites in New York State, In: Air Quality Meteorology and Atmospheric Ozone by, ASTM STP 653, Morris, A. L.; Barras, B. C.; Eds., American Society for Testing and Materials, p. 523-535, 1978.

night and replenished the following day by vertical mixing and limited photo-chemistry. [Coffey et al, 1978].

Concentrations aloft on Whiteface Mountain would not be expected to drop. By the time the ML reaches that altitude, it is reaching its maximum height for the day as solar radiation, and thus photo-chemistry and mixing also, begins to decrease. Thus, the ML reaches the top of Whiteface Mountain as ozone concentrations also peak. Since the mountain will soon lie in the RL, concentrations should be expected to remain relative constant until the next ML grows to that altitude or a new weather front begins to approach.

2.7 Typical Vertical Ozone Profiles and Their Significance

The ozone scavenging in the SBL and lack of production or depletion in the RL just discussed should result in a typical nocturnal ozone profile in which ozone concentrations drop to below 30 ppb near the ground, gradually increase with altitude up to the RL, remain constant in the RL, and then decrease in the free atmosphere. [Trainer et al, 1991; Nappo et al, 1989; Stull, 1988; Broder and Gygax, 1985; Ludwig, 1985; Wark and Warner, 1981; Harrison et al, 1978; and Van Dop et al, 1977]. The previous section provides both direct and indirect examples of such behavior. In another study, Van Dop et al [1977] made vertical ozone measurements at a rural site near Cabauw, The Netherlands. They observed a strong concentration

gradient from 100 micrograms/cubic (50 ppb) meter at the ground surface, to almost 200 micrograms/cubic meter (100 ppb) at 300 m. Concentrations were then constant until about 1900 m when concentrations began to fall again. The model Trainer et al [1991] used in their study also assumed a strong gradient from 20 ppb ozone at the ground to 120 ppb at 520 m above ground at the bottom of the RL. Concentrations then remain constant until about 900 m where concentrations begin to fall again as the profile enters the free atmosphere.

Other studies go beyond a few simple vertical profiles and show that ozone concentrations in the RL experience only a slight decrease. Broder and Gygax [1985] observed that ozone concentrations at 800 m above the bottom of the Reuss Valley decrease by no more than 20 ppb even with the additional ozone deposition associated with the katabatic flows in the Reuss Valley. In their examination of ozone data in New York City, Coffey et al [1978] show that nocturnal ozone concentrations at Roosevelt Island nearly always drop to near 0 ppb at night. However, 308 m higher on the World Trade Center, nocturnal ozone concentrations only drop when the Center is below the elevation of an inversion measured at Roosevelt Island [Coffey et al, 1978].

In an effort that verifies many of the impacts of the RL on ozone concentrations and ozone transport discussed so far, Ludwig [1985] compiled 286 ozone profiles made at varying times of the day and at varying positions relative to major

urban areas. Table 2-3 summarizes his work which describes the stages of development of a typical air mass and determined six different common profiles as shown in figure 2-10 [Ludwig, 1985]. Always, above the boundary layer in the free atmosphere the concentration stays roughly constant [Broder and Gygax, 1985, and Ludwig, 1985]. Likewise, in the study near Caubaw, the Netherlands, it was found "that over 2000 m the mean ozone concentrations in general scarcely vary with height until the tropopause is reached" [Van Dop et al, 1977]. However, Trainer et al [1991] assumed in their model that concentrations decreased slowly from the top of the EZ to the tropopause [Trainer et al, 1991].

An unpolluted air mass, especially one upwind of an urban area, is generally like profile A. With no precursors added during the day and after a SBL begins to forms profile A becomes profile B. The inversion has prevented ozone aloft from replacing ozone scavenged or deposited at the surface during the night. In a natural environment the profile would alternate between A and B [Ludwig, 1985]. Diffusion of ozone from the stratosphere and photochemical reactions with biogenic precursors would create a natural ozone concentration of 10-20 ppb during the day [Altshuller, 1987] throughout the ML [Ludwig, 1985]. Ground deposition would deplete the concentration at night [Broder and Gygax, 1985; Ludwig, 1985; and Harrison et al, 1978]. However, as a city adds pollution, profile A may become profile C before the air is completely

Table 2-3. Frequency of Typical Ozone Profiles by Common Locations

FREQUENCY OF OCCURRENCE PERCENT OF PROFILE TYPE BY TIME OF DAY AND LOCATION							
	Total	Profile Type					
Condition	Cases	A	B	C	D	E	F
Location:							
Upwind or to one side of city	49	38	4	7	18	14	18
Downwind of city	19	18	8	18	37	8	12
Above City	25	21	6	2	28	13	30
Time:							
06-09 LST	22	21	10	0	3	17	48
09-15 LST	56	40	3	9	25	11	13
15-21 LST	2	13	0	15	54	6	11
21-06	2	17	50	0	0	33	0

Source: Ludwig, F. L. Vertical Ozone Profiles in the Lower Atmosphere and Their Relation to Long-Range Transport. Presented: Ozone Symposium-Greece 1984; D. Reidel Publisher, p. 740-744. 1985.

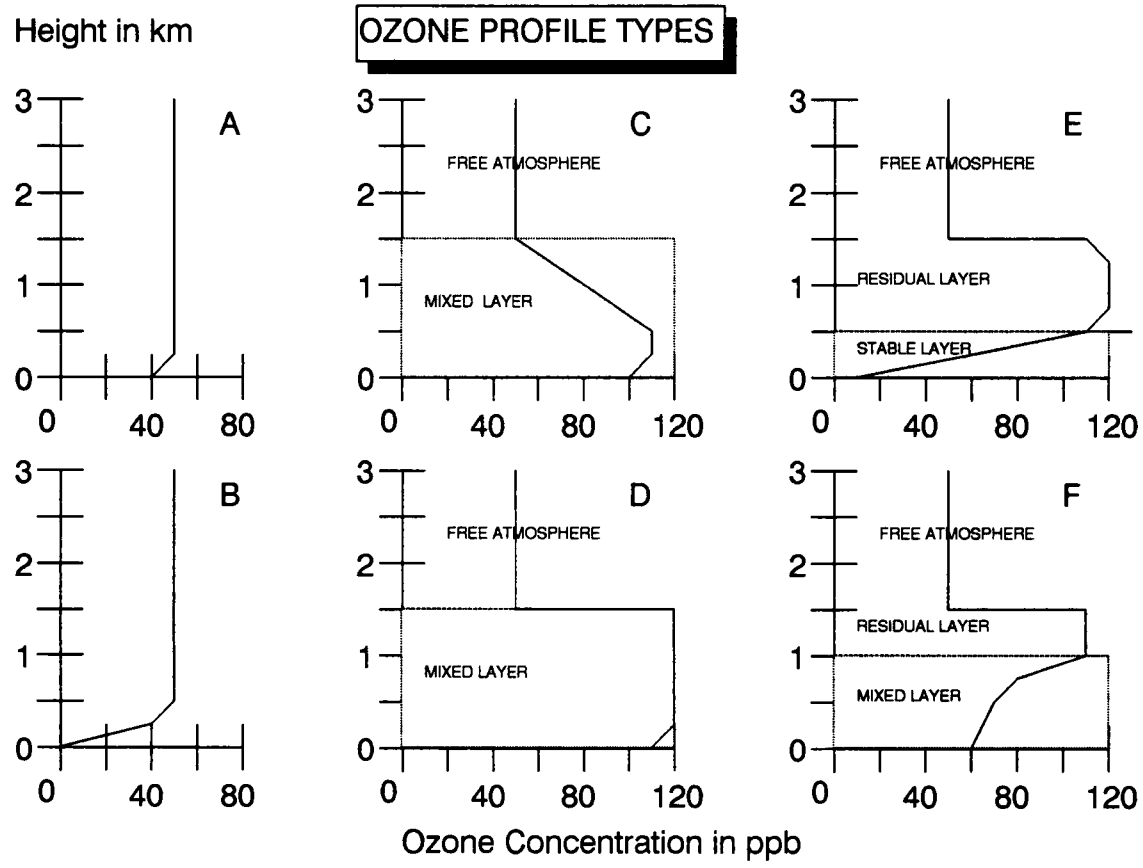


Figure 2-10. Typical Ozone Profiles

Source: Ludwig, F. L. Vertical Ozone Profiles in the Lower Atmosphere and Their Relation to Long-Range Transport. Presented at the Ozone Symposium-Greece 1984; D. Reidel Publisher, p. 740-744. 1985.

mixed in the ML. After more mixing the profile looks like D, where the concentration is constant and elevated throughout the ML but drops off as in a step function above the ML. With a strong SBL the profile changes to E by early morning just before sunrise. Concentrations in the RL remain high as in the day before, while the ground scavenges ozone at the bottom. As the ML grows from the ground surface on its way to become another profile D the profile will look like F. The new ML has a relatively constant concentration that is less than the previous day's concentration. As it mixes in air from aloft its concentration rises while the concentration at the height just included in the ML decreases [Ludwig, 1985].

2.8 Defining Residual Layer and Stable Boundary Layer Stations

As just discussed, there are many observations that attest to the consistency of high ozone concentrations in the RL and low concentrations in the SBL. Furthermore, there have been numerous observations of plumes staying intact for long distances in the RL or SBL and of the isolation of the RL from the effects of the ground surface. Thus, there is convincing evidence that ground level scavenging and deposition processes and topographical effects have, at best, only a limited impact on the RL. Thus, a monitor in the RL, like the one on Whiteface Mountain or the World Trade Center when it is above

the SBL, should not be expected to exhibit a diurnal cycle. Similarly, as shown in figure 2-11, observations on Mount Mitchell do not show a diurnal cycle. Considering that these two Mountains are well over 500 m over their surrounding terrain, then the air masses passing over stations on these ridges at night are not influenced by nocturnal ground level sinks and sources of ozone and its precursors. Since these stations have also observed concentrations of ozone that were over 120 ppb, it seems that they are in the boundary layer. Thus, they must be impacted by air from the RL and not the SBL and could provide important data about RL ozone concentrations. Since these monitors are also on a ground (ridge top) surface, there may be some confusion if lower altitude stations are called ground surface monitors. Also, lying on a ridge top may not be sufficient evidence to show that one is monitoring the RL since the ridge top may in fact be covered by the SBL as the World Trade Center often is. Thus, in this thesis the name *Residual Layer Monitors or RL Stations* will refer to those stations high enough to predominately lie in the RL during the night. In future analysis, such stations should be recognizable by a definitive lack of a diurnal cycle and a high elevation. All other stations will be considered *Stable Boundary Layer Monitors* or *SBL Stations.*

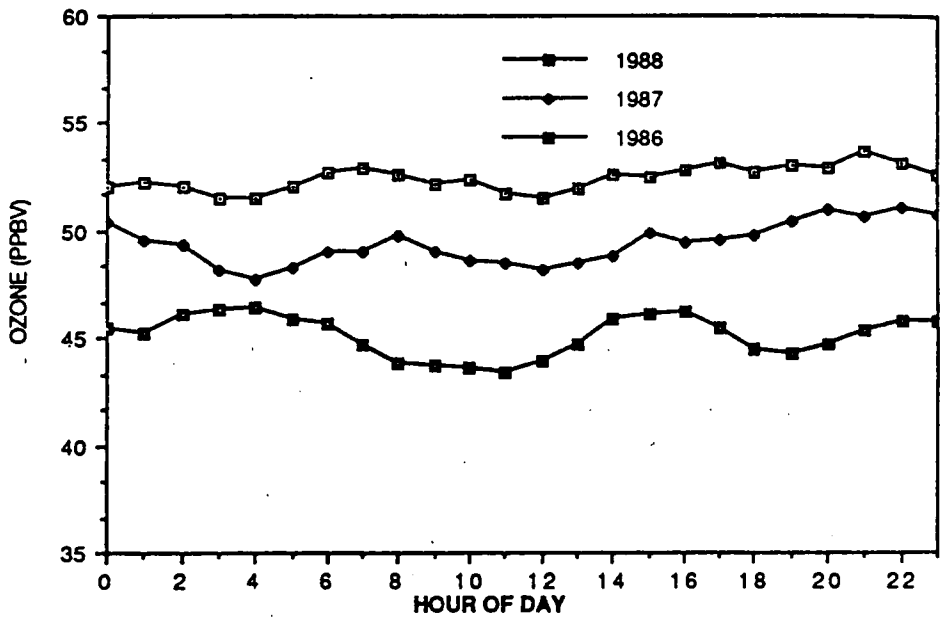


Figure 2-11. Typical Ozone Concentrations on Mount Mitchell, North Carolina.

Source: Aneja, V. P.; Businger, S.; Li, Z.; Claiborn, C.; Murthy, A. Ozone Climate at Mt. Mitchell, North Carolina, and Its Association with Synoptic Events. For Presentation at the 82nd Annual Meeting and Exhibition, Air and Waste Management Association. Publication: 89-35.6. 1989.

2.9 Area-wide Ozone Concentrations Move with High Pressure Systems

Coffey et al [1978], observed that anthropogenic emissions seem to spread over large areas of at least several hundred square miles. Furthermore, while their measurements at Whiteface Mountain did not show any urban plumes, they did not rule out the possibility that "[A]nthropogenically generated ozone, with its precursors well diluted, may cause a fraction of the ozone at Whiteface. [Coffey et al, 1978]" However, they offer no explanation of these processes.

The study by Colbeck and Harrison [1985] of rural ozone levels near Lancaster England which were not directly affected by the urban area implies the same idea. They correlated high pressure systems' origin and the daily ozone maximums while their sites were under these anti-cyclones. Essentially, they found that the cleanest systems came from the ocean and the most polluted came from continental sources, as shown in table 2-4 [Colbeck and Harrison, 1985]. The author of this thesis has added the column of concentration averages combining 1982 and 1983.

This article certainly implies that pollutants can build up in large air masses as wind distributes the anthropogenic emissions throughout the high pressure system, raising the background concentration. The logical layers to store these high concentrations as the winds mix the entire anti-cyclone

Table 2-4. Air Mass Classification and Ozone Levels, May-September 1982 and 1983, near Lancaster England

Air mass classification and ozone levels May-September 1982 and 1983					
	1982		1983		1982, 1983
Air Mass	Number of days	Concentration[1]	Number of days	Concentration[1]	Weighted Concentration
Polar maritime	33	41.5	31	50.6	45.9
Arctic maritime	16	50.7	14	60.4	55.2
Arctic continental	5	40.9	7	76.4	61.6
Polar continental	9	66.5	8	79.9	72.8
Tropical continental	20	73.4	12	69.0	71.8
Tropical maritime	18	55.6	19	50.4	52.9

[1] Average of maximum hourly ozone concentration (ppb).

Source: Colbeck, I.; Harrison, R. The Frequency and Causes of Elevated Concentrations of Ozone at Ground Level at Rural Sites in North-West England. Atmospheric Environment. 19(10): p. 1577-1587. 1985.

and as the system moves across the ocean would be the ML and the RL.

In the United States G. D. Wight et al studied typical high pressure systems from April 1 to September 30, 1976, that moved from Canada into the midwest, stayed in the midwest or northeast for several days, and then moved out of the region. The average concentration of ozone in the anti-cyclone was 30 to 50 ppb when it entered from Canada. Some of their conclusions follow

> " 4. ...the locations which first experienced ozone levels above 80 ppb were immediately downwind of urban and industrial sources.
>
> 5. As the high pressure system moved eastward, the areas of high ozone concentration intensified, expanded, and eventually merged. After several days in the United States most of the areas under the influence of the high pressure system experienced ozone levels in excess of 80 ppb.
>
> 6. On subsequent days, areas of elevated ozone merged, but 'urban plumes' of more elevated ozone remained detectable downwind of midwest and northeastern urban centers.
>
> 7. Fairly uniform elevated ozone concentrations were noted over broad areas by the time the east coast was on the backside of the high.

8. The highest concentrations were found downwind of urban areas in the Northeast at times when the air flow directions was such that urban plumes were superimposed on substantially elevated air mass-borne ozone concentrations on the backside of the high pressure system.

9. A cold front marked the end of the episode and provided a clear demarcation between the ozone-laden air mass and a new, cleaner air mass as it traveled from west to east."

G. D. Wight also reported from other sources that the half life of ozone "above the nocturnal inversion layer (and away from sources of oxides of nitrogen) [is] 16 to 34 h" with another reported average of 29.4 h [Wight et al, 1978]. These half lives are important because they provide time for winds in the RL to mix and regionally transport ozone before it decays. They also report an event in August of 1976 in which air reaching the New York City area from the Midwest brought a background concentration of between 100 and 125 ppb. Sources along the East Coast added at least 80 ppb more ozone to this air mass [Wight et al, 1978]. From the figures in this article one gets the impression of a high pressure system as being like a bubble in the atmosphere. Instead of individual factories being point sources, whole urban areas become sources which emit into this bubble. The geostrophic

winds then mix these pollutants throughout the bubble. If the bubble stays in one place, the plumes will grow, expand and merge with one another. However, when the bubble moves, it carries the pollution laden air and plumes with it.

2.10 Summary and Conclusions

Together these articles suggest a likely scenario for episodes of high ozone concentrations, especially in rural areas and medium sized cities. As a high pressure system or other air mass moves over land it will accrue biogenic and anthropogenic emissions. Depending on the length of time it travels over areas of high emissions and the emissions rates, it may build up a considerable concentration of ozone and its precursors. However, the diurnal cycle at SBL stations masks the buildup of pollution in the anti-cyclone as the strong stability of the SBL allows surface deposition and nitrogen oxide scavenging to deplete ozone concentrations in that layer. However, the clear skies inherent in strong high pressure systems also create a moderately stable RL which does not experience the nocturnal depletion of ozone. Instead it is a night-time reservoir of pollution that can travel many miles un-inhibited by topographical effects. In fact from the viewpoint of a SBL monitoring station the following day, it is often a substantial source of ozone. Thus, the RL plays an active role in dispersing urban pollutants over areas of

hundreds of square miles within the airflow of a high pressure system. Thus, some high ozone concentrations, including some higher than 120 ppb, could be expected in rural areas in the RL contributes far more ozone than photochemistry of locally emitted precursors. Unfortunately, adequately monitoring of this situation requires monitors in the RL, normally an expensive proposition requiring towers greater than 500 m high, extensive airplane monitoring, or tethered balloon data. However, many ridges in the Appalachian chain appear to be high enough and isolated enough to be impacted by the RL instead of the SBL.

3.0 STATEMENT OF OBJECTIVES

At the time this thesis was written, Knoxville Tennessee had recently been declared as re-attainment status for the Ambient Air Quality Standard for ozone (AQS for ozone). However, any city the size of Knoxville in the Eastern United States has the potential to violate the ozone standard. Practical emissions abatement programs for the AQS for ozone must know the background ozone concentrations and must consider a typical scenario that may lead to an exceedence of the AQS for ozone. Thus, this thesis attempts to characterize the typical meteorological conditions and ozone concentrations for high ozone concentrations episodes in East Tennessee.

Based on information presented in the Literature Review it is evident that a characterization of ozone episodes in East Tennessee should examine several contributing factors related to high pressure systems and the residual layer. In order to determine the impact of high pressure systems the different ozone episodes will need to identified and labeled. After determining the high pressure system influencing Knoxville during each episodes, back trajectories can be constructed and categorized according to routes. The maximum concentrations observed during each episode can used to quantify the effects of each high pressure system and route by calculating an average maximum concentration associated with each route type.

Data can be assembled from high altitude stations (residual layer stations) with characteristics similar to Whiteface Mountain and Mount Mitchell. In fact, the latter data is available for studying ozone around East Tennessee. Data from these stations can be collected for several episodes and compared with each other, nearby stable boundary layer stations, and Knoxville ozone concentrations to determine any possible relationships. Lastly, isopleth maps of ozone concentrations throughout the Southeast can be constructed and related to the corresponding high pressure system and residual layer data. Such a comprehensive approach should determine the importance of the residual layer to ozone concentrations in the East Tennessee area.

4.0 DATA COLLECTION

4.1 Ozone Monitoring Station Locations and Characteristics

Ozone data for the Knoxville area are available from seven pollution monitoring stations as shown on the map in figure 4-1 and described in table 4-1: Nances Grove, East Knox Elementary, Spring Hill Elementary, Alcoa Highway, Freels Bend, Look Rock, and Cove Mountain. East Tennessee's geography plays an important part in the placement of these monitoring stations. Knoxville lies in the Great Valley that extends from Pennsylvania to Alabama. In Tennessee the Cumberland Plateau forms the western boundary and the Unaka and Great Smoky Mountains the eastern boundary. The Great Valley and the many smaller ridges that dissect it are aligned southwest to northeast, forcing wind profiles and plume effects near the ground and in the SBL into these channels. During the summer the dominant wind direction, as measured at the standard 10 meter height, is out of the Southwest. The various agencies that monitor ozone around Knoxville have used these facts to choose upwind, downwind, and background stations.

As the station nearest the urban core, Spring Hill Elementary provides the best data for urban Knoxville. Considering the southwesterly wind pattern, the Freels Bend Site is considered the upwind station to determine concentrations before they reach Knoxville, while East Knox

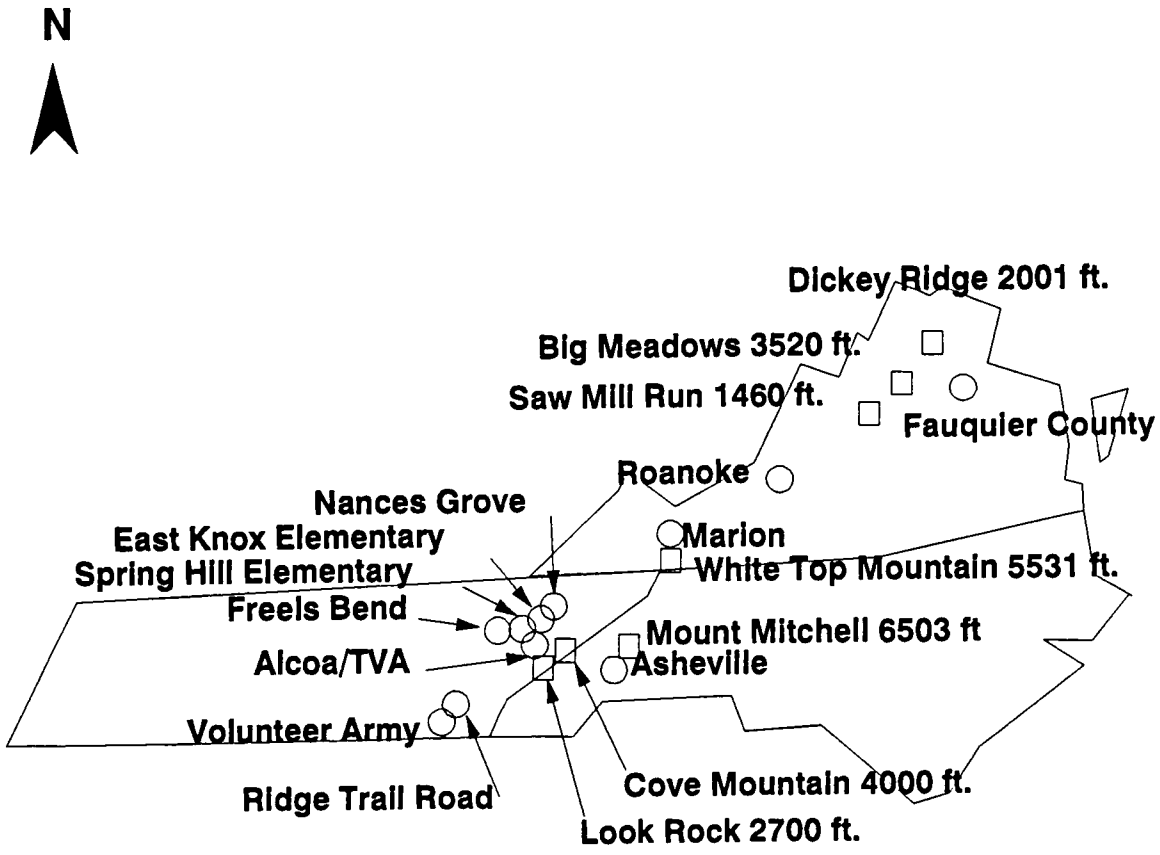


Figure 4-1. Ozone Monitoring Stations Intensely Studied

Table 4-1. Knoxville Area Ozone Stations, General Information

Station	Operator	Responsible Agency	Dir./ Miles from Knoxville	Years of Opera -tion
East Knox Elementary	Knox Co. Air Labs	Knox Co. Air Labs	NE 2	1988-1992
Spring Hill Elementary	Knox Co. Air Labs	Knox. Co. Air Labs	Near Urban Core	1988-1992
Nances Grove	UT Envir. Eng.	Tenn. Dep. of Air Pol. Control	NE 25	1992
Freels Bend	UT Envir. Eng.	Tenn. Dep. of Air Pol. Control	W 5	1992
Alcoa Highway	UT Envir. Eng.	TVA	S 34	1991-1992
Look Rock	Great Smoky Mt. Nat. Park	Great Smoky Mt. Nat. Park	S 33	1988-1992
Cove Mountain	Great Smoky Mt. Nat. Park	Great Smoky Mt. Nat. Park	S 33	1988-1992

Elementary and Nances Grove should show any plume effects from Knoxville. Originally the Alcoa station was chosen to be a background station to one side of the city. However, after examining data to include in this thesis, it is apparent that maximum concentrations are quite consistent over the entire valley and it is hard to pinpoint an exact plume from Knoxville. Therefore, these stations apparently do not quite function in the idealized manner just presented. Of the stations in the immediate vicinity of Knoxville, only the Alcoa station is not on the EPA's AIRS, Areometric Information Retrieval System.

Of these five valley stations, only Nances Grove has a strong tendency to have nocturnal ozone concentrations as high as 30 or 40 ppb. The cause may be due to the station being on a broad hill overlooking the Holston River Valley that does not experience as strong a SBL as other stations. The Spring Hill Elementary station may experience NO_x scavenging due to its proximity to urban roads. Three others experience strong drainage flows: the Alcoa and Freels Bend sites lie next to Fort Loudon and Melton Hill lakes; and the East Knox Elementary station lies at the base of House Mountain.

The National Park Service chose Look Rock and Cove Mountain to study ozone concentrations coming into the Great Smoky Mountains National Park from the valley as a whole, with a particular interest in any plumes from Knoxville. As high altitude stations they also provide insight into the

background concentration aloft in the RL near Knoxville. The additional weather data collected at these sites provides insight into the meteorological parameters that help determine ozone concentrations.

Figure 4-1 also shows several other important RL stations used in this regional ozone analyses: Mount Mitchell, White Top Mountain, Saw Mill Run, Big Meadows, and Dickey Ridge. Because of their high altitude these stations act like the Great Smoky Mountain stations and provide insight into ozone aloft. Important summary data for all the high altitude stations is included in Table 4-2. Substantial supporting data also comes from several SBL monitors which often lie near one of the high altitude stations: Asheville, North Carolina, Fauquier County, Virginia; Roanoke, Virginia; Marion, Virginia; and Chattanooga, Tennessee. The stable layer monitors are those that lie in the SBL. Consequently they are not usually on ridge tops.

The higher altitude stations, or RL stations, (White Top, Mount Mitchell, Dickey Ridge and Big Meadows) are high enough to usually lie well above the nocturnal inversion, do not experience as many local effects, and are better indicators of regional transport and background concentrations. In general this research finds these effects more prominent the higher in elevation the site is. However, Dickey Ridge is located toward the end of a ridge at the north end of the Shenandoah National Park. Consequently, it has the potential for

Table 4-2. Residual Layer Ozone Stations, General Information

High Altitude Station	Feet above Mean Sea Level	Location	Nearby Landmarks	Years of Operation	Nearest Valley or Low Altitude Station
Mount Mitchell[1]	6503	Yancey Co. NC	Asheville, NC	1988-1992	Buncombe Co. NC
White Top Mountain[1]	5531	Smyth Co. VA	Mount Rodgers Nat. Recreation Area	1988	Marion VA
Saw Mill Run	1460	Augusta Co. VA	Shenandoah Nat. Park	1988-1992	Roanoke VA
Big Meadows	3520	Madison Co. VA	Shenandoah Nat. Park	1988-1992	Roanoke VA Fauquier Co. VA
Dickey Ridge	2001	Warren Co. Va	Shenandoah Nat. Park	1988-1992	Fauquier Co. VA
Look Rock	2700	Blount Co. TN	Great Smoky Mountains Nat. Park	1988-1992	Knoxville TN
Cove Mountain	2700	Sevier Co. TN	Great Smoky Mountains Nat. Park	1988-1992	Knoxville TN

[1]Mount Mitchell was first put on AIRS in 1992 when the North Carolina State Government took it over. In 1988 both Mount Mitchell and White Top Mountain were part of the Cloud Physics Experiment.

exposure to plumes from the Washington D.C. Metropolitan Area. Therefore, even though it is lower in elevation than Big Meadows, it experiences higher ozone concentrations as if it had a higher elevation.

Unfortunately, their are few other reliable RL stations in the Southeast available on AIRS. One problem is that the height of the SBL makes building a tower too inconvenient and costly to consider. Airplane or tethersonde data is usually associated with intensive research efforts which may or may not occur during periods of high ozone concentration and which are not normally reported on AIRS. Thus the relatively narrow Appalachian Chain provides the only sites in the Southeast for stations to monitor the RL on a continuous basis. Furthermore, the scarcity of large metropolitan areas in the Appalachian region tends to reduce the number of monitoring stations. The stations that are available are generally placed by National Park or National Forest officials or by scientific researchers.

4.2 Ozone Monitoring Data Quality

The USEPA has designated AIRS as its official computer repository for ambient air pollution raw concentrations, summary tables, and monitoring information. The database is used for research, modeling, and determining compliance with ambient air quality standards. Thus, EPA requires that all

data input into the system follow a rigorous quality control and assurance program to lessen the conflict between these two groups. As shown in table 4-1, most of the local stations are in AIRS and have strong quality assurance programs. Of the stations examined intensely for this thesis, only two were not available on AIRS: the Alcoa station and any data from Mount Mitchell before 1992 when the state of North Carolina began operating the station. The Alcoa station data were obtained because the station is operated for the Tennessee Valley Authority, TVA, under a contract to the University of Tennessee's Department of Civil and Environmental Engineering. As one can see from table 4-3, TVA uses a quality assurance program at the Alcoa station comparable to the other local stations that are part of the AIRS network. The State of North Carolina Division of Air Pollution Control provided the author a copy of the Mount Mitchell Data upon his request. In conversations with officials from the TVA and the State of North Carolina, the author of this thesis learned that the Mount Mitchell and White Top stations were part of the Mountain Cloud Physics Experiment. Also although the Mount Mitchell site was not certified as an EPA approved monitoring station, the State of North Carolina said that the audits performed by outside agencies of the then current monitoring system showed excellent results. Furthermore, for episodes examined in this thesis and considering the evidence presented in this thesis, events with similar characteristics were

Table 4-3. Knoxville Area Ozone Monitors, Data Quality and AIRS status.

Station	Auto. Daily Zero/Span	Weekly Level One, Precision Check	Auditors	Input to AIRS
East Knox Co. Elementary	No	Yes	Tenn. Dep. of Health	Yes
Spring Hill Elementary	No	Yes	Tenn. Dep. of Health	Yes
Nances Grove	Yes	Yes	Tenn. Dep. of Health	Yes
Freels Bend	Yes	Yes	Tenn. Dep. of Health	Yes
Alcoa Highway	Yes	Yes	Tenn. Dep. of Health	No
Look Rock	Yes	Yes	Tenn. Dep. of Health	Yes
Cove Mountain	Yes	Yes	Tenn. Dep. of Health	Yes

occurring simultaneously at White Top Mountain, Dickey Ridge, Big Meadows, and Saw Mill Run; and this thesis provides a reasonable explanation for these events at these ridgetop stations.

4.3 Other Data Sources and Quality

The regional ozone data used in the ozone isopleth maps was compiled from AIRS Raw Data Reports. For an additional quality check, the data from these reports were compared to data from the AIRS Quick Look Report, which records the ten highest ozone concentrations for each station requested. If, on a given day at a particular station, the maximum value listed in the Raw Data Report was higher than the maximums listed in the Quick Look Report, that day at that station was removed from the inventory for this thesis. When a substantial amount of the days violated this criteria at a single station, all of that station's data were removed. Thus, several stations in Fairfax County Virginia and all stations in South Carolina were excluded.

The weather data used in this thesis comes from various sources. Data for tracking high pressure systems and calculating geostrophic winds comes from the Daily Weather Maps, published by National Oceanic and Atmospheric Administration, NOAA. Other weather data comes directly from

the National Weather Service, which is a branch of NOAA, or the various pollution monitoring stations.

5.0 IMPACT OF HIGH PRESSURE SYSTEMS ON OZONE EPISODES AROUND KNOXVILLE

5.1 Definition of an Ozone Event and Ozone Episode

The ozone concentrations around the Knoxville metropolitan area of greatest importance are those that are greater than 120 ppb. Table 5-1 is a list of such days that appear on the USEPA AIRS for the two stations near Knoxville, East Knox Elementary and Spring Hill Elementary. Each of the days in this table defines one ozone event of interest.

As Figure 5-1 demonstrates, ozone events around Knoxville are not isolated random occurrences. In fact, these plots of the daily maximum concentrations for these two stations for the months of June, July, and August of 1988, 1989, and 1990 are much like a wave with an average period of five to eight days and a maximum peak-to-peak amplitude of over 60 ppb. As noted in the Literature Review, ozone is expected to be highest during warm, sunny, days, particularly those under the influence of a high pressure system. Furthermore, one would expect the lowest concentrations during the passage of low pressure systems and cold fronts as these cloudy events prevent further photochemistry and also dilute ozone concentrations with an increase in the effective mixing height and turbulence. Thus, it becomes apparent that an ozone episode begins as a new high pressure system moves into an area and ends when it is replaced by another anti-cyclone.

Table 5-1. Ozone Concentrations at or Greater Than 120 ppb around Knoxville.

	Date	Concentration	Station
1.	7/9/88	150	Spring Hill
-	7/9/88	145	East Knox
2.	6/22/88	140	East Knox
3.	6/24/88	140	Spring Hill
-	6/24/88	135	East Knox
4.	7/9/90	135	East Knox
-	7/9/90	120	Spring Hill
5.	6/15/88	135	East Knox
-	6/15/88	130	Spring Hill
6.	8/18/88	135	East Knox
7.	6/28/90	123	East Knox
9.	8/18/90	120	Est Knox
-	8/18/90	120	Spring Hill
10.	6/27/90	120	East Knox
11.	7/10/88	120	East Knox
-	7/10/88	120	Spring Hill
12.	8/26/88	120	East Knox
-	8/26/88	120	Spring Hill
13.	7/8/88	120	Spring Hill

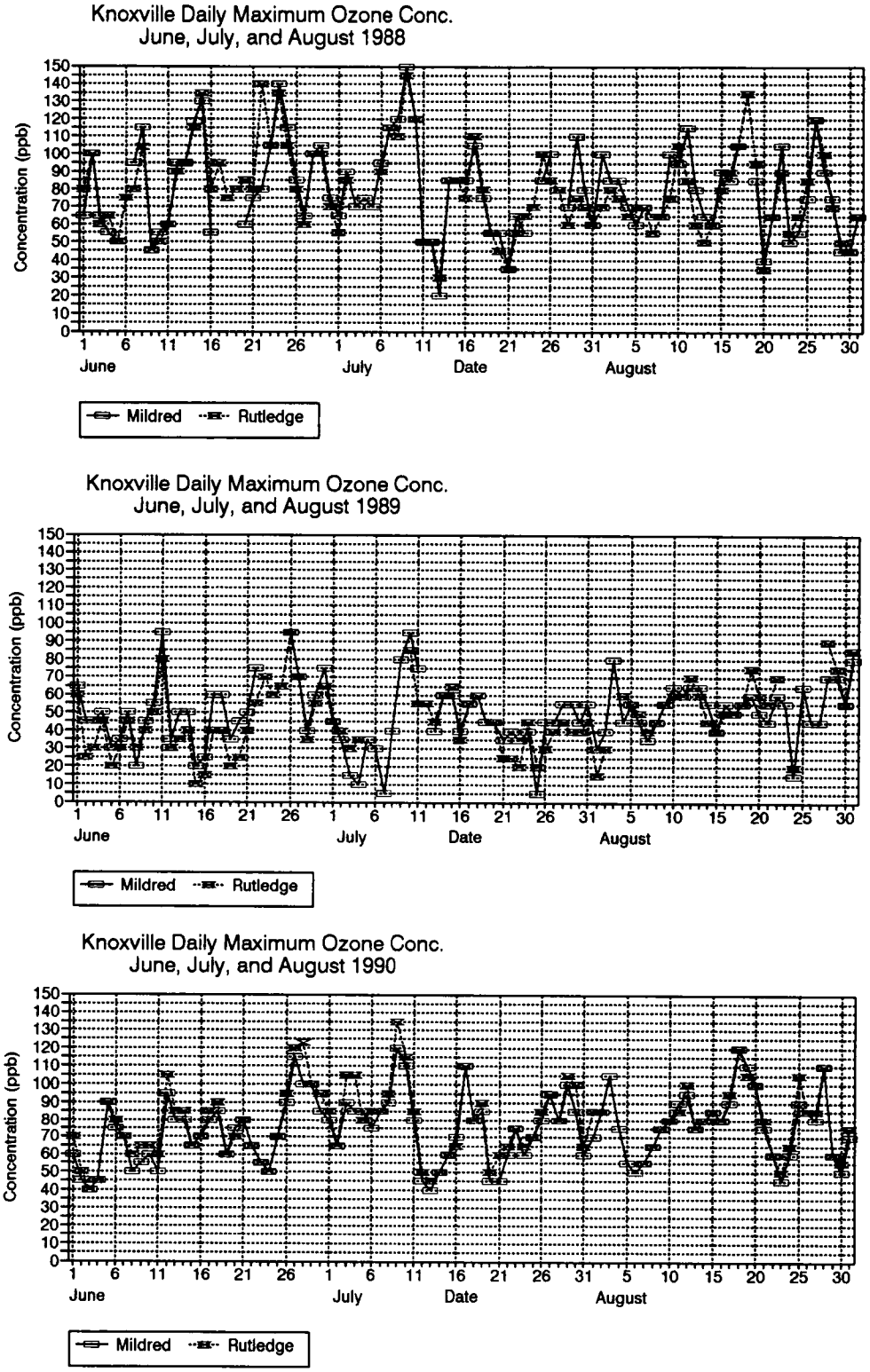


Figure 5-1. Knoxville Daily Maximum Ozone Concentrations June, July, and August of 1988, 1989, 1990.

Table 5-2 compiles the dates of the maximum concentrations between each major trough for June, July, and August for 1988, 1990, and 1991 as graphed in figure 5-1. Consequently, it represents an estimation of the number of different ozone episodes and labels them by the maximum ozone concentration date and value. Since figure 5-1 shows that the highest ozone concentration for June, July and August of 1989 was less than 100 ppb, and since this research is primarily interested in factors that contribute to ozone concentrations greater than 120 ppb, ozone data from 1989 received no further consideration in this thesis.

5.2 Procedure for Correlating Ozone Episodes and High Pressure System Trajectories

Starting with a date listed in table 5-2 or graphed in figure 5-1, it was possible to locate the high pressure system on the NOAA Daily Weather Maps which most likely influences East Tennessee on that date. Then, backing through time, one day at a time, the route that the Anti-Cyclone took to arrive at its current location was determined. Once a high pressure system route has been plotted the associated episode is referred to by the date of the maximum concentration, as in those concentrations listed in table 5-2. It is then possible to classify these events into route types, find the average concentration by route type, and then draw conclusions. Each of these episodes is graphed and sorted by route type and

Table 5-2. Episode Maximum Ozone Concentrations and Date

DATE 1988	ppb OZONE	DATE 1990	ppb OZONE	DATE 1991	ppb OZONE
6/2	100	6/5	90	5/18	87
6/8	115	6/12	105	5/24	86
6/15	135	6/18	90	5/31	90
6/22 6/24	140	6/21	80	6/10	99
6/29	105	6/28	123	6/14	73
7/9	150	7/3 7/4	105	6/18	86
7/17	110	7/9	135	6/21	73
7/25 7/26	100	7/17	110	6/29	78
7/29	110	7/29	105	7/2	85
8/1	100	8/3	105	7/7	95
8/11	115	8/12	100	7/11	89
8/18	135	8/18	120	7/16	83
8/22	105	8/25	105	7/22	100
8/26	120	8/28	110	7/30	100
				8/7	105
				8/17	105
				8/24	105
				8/29	100

date in Appendix A as forward trajectory beginning the first day the high pressure system appears in or near the United States and ending on the episode's maximum concentration date.

The procedure for determining the high pressure air mass routes for the dates in table 5-2 used several items from the Daily Weather Maps: the location of the listed high pressure air masses as noted by "HIGH" or "H," the 500 millibar contour chart, the isobars around these high pressure systems, and some event specific estimations. Starting with a date from table 5-2, the nearest high pressure air mass that influences East Tennessee on the day in question was picked. Next the anti-cyclone's position the previous day was located by following the contours of the previous day's 500 millibar contours, which are parallel to the wind directions at that height. Normally, it is possible to start with the current position and go back to another marked high pressure system the previous day. A quality assurance check included examining the surface pressure contours and checking that the successive positions do not create a change in pressure more than 4 millibars and that changes in isopleth shapes can be explained by the meteorological circumstances. For instance a strong hurricane moving northeast off of the North Carolina coast may push part of a high pressure air mass in New York or Pennsylvania to the south west. In other instances anti-cyclones appear to form or strengthen with no apparent surface predecessor. However, these maps often show a stagnant high

pressure at the 500 millibar height, which may be subsiding enough to increase pressure below the 500 millibar height on the Earth's surface. During a few events it was impossible to create a forward trajectory for the most influential high pressure system as it was not apparent. These special cases have been listed in Table 5-3.

5.3 Conclusions from Correlating Ozone Episodes and High Pressure System Trajectories

From these trajectories this author has named the following high pressure pathways.

1) The Mid-Westerner. It originates north or northwest of Tennessee in Canada or the Pacific Northwest and eventually moves off into the Atlantic Ocean. It rarely moves south of Tennessee, and some never leave Canada. Many of them leave the U. S. Mainland from New England.

2) The Westerner. It moves in from the west or southwest and then eventually moves out into the Atlantic.

3) The Colonist. This is a Mid-Westerner that instead of moving off into the Atlantic after reaching the coast, will move south along the Appalachian Mountains or the Atlantic Seaboard. However, the one exception is the July 9, 1988, episode, which could only be traced up the Appalachians to a

Table 5-3. Dates for which no High Pressure Trajectory Was Included

Dates			Reason for Exclusion from Table 4-3
6/8/88			Route stagnated northwest of Tennessee and did not meet the definitions of any of the route categories
7/17/88	8/26/88	7/3/90	Unable to determine trajectory
5/18/91	6/18/91	6/21/91	
7/7/91	7/30/91		

location north east of Maine and not back across Canada or the Midwest.

4) The Gulf Wanderer. These high pressure systems stay in and around the Gulf of Mexico for several days and could not be traced to the U. S. mainland or the Atlantic Coast.

5) The Returnee. This is a Colonist that moves from the Atlantic Ocean into the Gulf States or the Gulf of Mexico. Since its average maximum concentration is about the same as the Gulf Wanderer's and since the last leg of the Returnee's path is very similar to the Gulf Wanderer's, these are probably the same path.

6) The Mountain Squatter. These high pressure systems have stagnated for several days just to the North or Northeast of Tennessee in Kentucky, West

Virginia, or Virginia, and could have followed any of the above routes to its current location.

7) The Coastal Squatter. These high pressure systems have stagnated for several days just to the East of Tennessee in the Carolina's or the Atlantic Ocean and could have followed any of the above routes to its current location.

Table 5-4 shows the maximum concentrations for each episode grouped by high pressure route type and the average maximum ozone concentration for each route type. The top three route types have no stagnating properties, while the bottom trajectories represent stagnated air masses in which the highest pressure system may roam randomly over several states without being replaced by any new air mass. Table 5-3 shows those dates from table 5-2, the original estimation of ozone episodes, which are not included in table 5-4, the final list of ozone episodes.

Table 5-4 also includes dates that indicated a probable maximum if an air mass had not stagnated and been replaced by another system. This was assumed to be the maximum concentration date within one day of when such an air mass began to stagnate. These dates are indicated by an asterisk in the table and are not graphed separately in appendix A. Note that when one of these dates corresponded to a trough in figure 5-1, then that date was not included in this table.

Table 5-4. Maximum Ozone Concentrations by Episode and High Pressure Route Type

MID-WESTERNER		WESTERNER		COLONIST	
Date	Max	Date	Max	Date	Max
7/29/88	110	5/12/92	112	8/25/90	105
6/29/88	105	7/17/90	110	8/29/91	100
8/22/88	105	7/29/90	105	5/23/92	97
6/12/90	105	7/25/88	100	7/6/88[1]	95
7/3/90	105	8/12/90	100	6/18/90	90
8/3/90	105	6/26/90[1]	95	5/29/91[1]	65
8/17/91	105	6/20/88[1]	85	5/22/91[1]	60
6/12/88[1]	95	8/15/90[1]	85		
7/8/90	95				
6/5/90	90				
7/7/92	84				
7/16/91	83				
6/8/91[1]	80				
average	98	average	99	average	87
number of events	13	number of events	8	number of events	7

GULF WANDERERS AND RETURNEES		MOUNTAIN SQUATTER		COASTAL SQUATTER	
Date	Max	Date	Max	Date	Max
6/24/88	140	7/9/88	150	6/22/88	140
8/18/88	135	8/18/90	120	6/15/88	135
7/9/90	135	8/11/88	115	6/28/90	123
7/13/92	107	8/28/90	110	7/20/91	92
8/7/91	105	8/24/88	105	5/24/91	86
7/22/91	100	6/2/88	100	6/29/91	78
5/31/91	90	8/1/88	100		
7/11/91	89	6/10/91	99		
		7/2/91	85		
average	113	average	109	average	110
number of events	8	number of events	9	number of events	6

[1] Date represents the maximum concentrations just before the high pressure system stagnated. These dates are not graphed in Appendix A.

A comparison of the dates in table 5-2 of estimated episodes, table 5-4 of the actual episodes, and the maps in appendix A validates the proposed definition of an ozone episode, which extended from trough to trough in the daily maximum ozone concentrations in figure 5-1. Although table 5-3 shows that not all high ozone concentrations have an associated anti-cyclone with a clearly defined trajectory, the list of exceptions is quite short. Thus, there is clearly a high pressure system associated with most ozone events and episodes. Furthermore, only nine high pressure systems contributed to more than one ozone episode. In at least one case the two episodes were separated by a third intervening episode and anti-cyclone. The others show days of weakening influence during the transition from one episode to another. Some of these situations were caused by the system having less influence as it temporarily moved away from East Tennessee. Other drops in concentration came as a low pressure disturbance or weak frontal system passed through East Tennessee that disintegrated without completely replacing the original air mass. Thus, daily maximum ozone concentrations seem to increase as a high pressure air mass moves into the East Tennessee area and stagnates; the daily maximum concentrations then decrease as the influence of the anti-cyclone weakens.

Since the maximum difference between route averages is only 26 ppb, the route the air mass takes to reach East

Tennessee probably has an insignificant relationship to ozone concentrations around Knoxville. One explanation is that Knoxville is surrounded by metropolitan areas that have had difficulties complying with ambient ozone standards or have large concentrations of people. These areas include Atlanta, Nashville, Louisville, Cincinnati, Pittsburgh, Ashland Kentucky-Huntington West Virginia, Washington D.C., Norfolk-Portsmouth-Virginia Beach, the North Carolina Triad, and Charlotte.

Consequently, Knoxville contrasts with the British Isles since the latter is often impacted by air masses originating in and traveling through maritime conditions with few sources of ozone precursors. Unlike the English results, an analysis of anti-cyclone route directions for East Tennessee does not indicate a particular source area that contributes high background concentrations of ozone or its precursors.

However a comparison of the non-stagnating routes: the Westerner, the Mid-Westerner, or the Colonist, and the stagnating route types: the Gulf Wanderer, the Returnee, the Mountain Squatter, and the Coastal Squatter, reveals a striking difference -- all of the ozone exceedences in table 5-4 occur during stagnant air masses. Ozone concentrations in the other three routes have not exceeded 112 ppb ozone, much less exceeded the AQS of 0.12 ppm (125 ppb). Thus, stagnation would appear to be a necessary meteorological condition for an exceedence of the ozone AQS for East Tennessee. Furthermore,

as noted earlier, these exceedences are not random occurrences; daily maximum concentrations in East Tennessee usually rise or decay over several days, even though anthropogenic emissions are assumed to be relatively constant during the week or weekend. While this phenomenon may be related to changes in mixing height and temperature, storage of ozone in the RL may also be of importance. However, ascertaining the RL's impact requires ozone data from that part of the boundary layer. As noted in the literature review, the RL frequently has higher ozone concentrations than the ML underneath and could even account for long range transport or storage when ground level stations observe nocturnal concentrations near zero ppb.

Thus, this research has found that ozone concentrations increase as a high pressure air mass begins to be the primary meteorological influence for East Tennessee. Furthermore, it seems that exceeding the AQS of 0.12 ppm (125 ppb) requires the high pressure system to stagnate. Although the RL may have an important role, more research is needed to clarify its significance. The following sections compares data from low and high altitude ozone stations to determine the impact of the RL on ozone concentrations in East Tennessee.

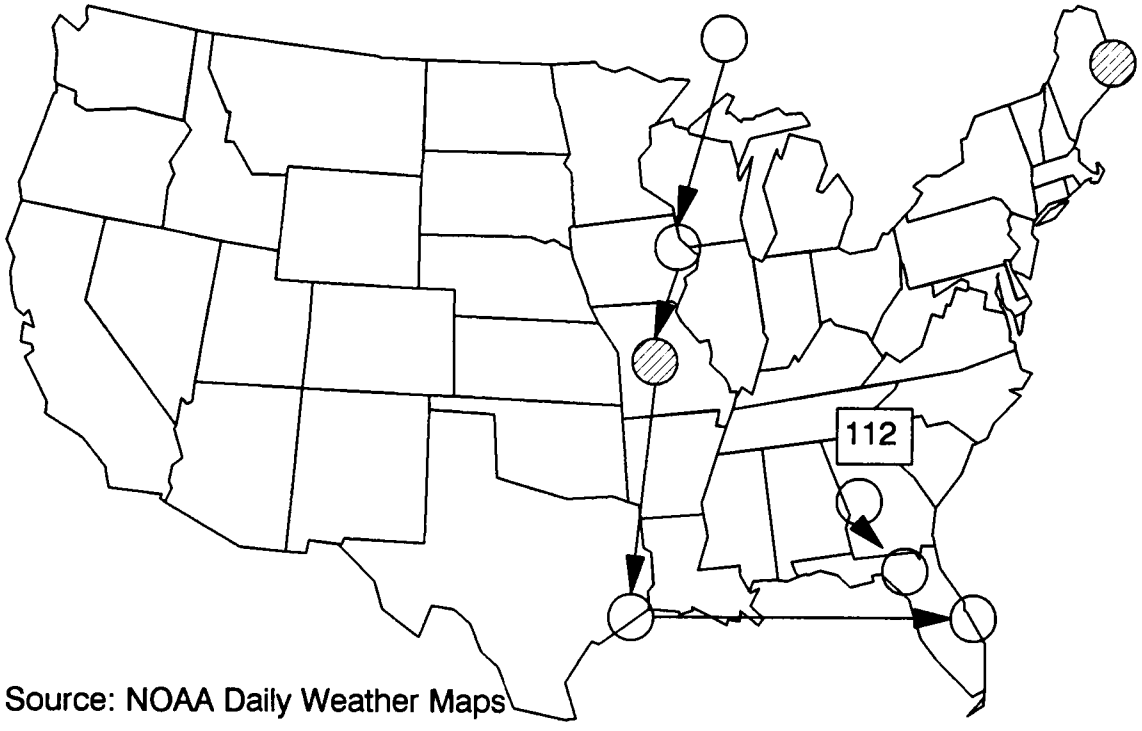
6.0 MAY 8-13, 1992

This event was chosen because it provides a dramatic example of the role of the RL in the regional transport of ozone. For several days through May 8 1992, East Tennessee had been experiencing rainy weather. However, on May 9, the weather began to clear as a high pressure system moved in from the west, but ozone concentrations remained low during the day. That night the SBL stations all experienced a normal drop in concentration to near zero ppb. However, two RL stations near Knoxville, Look Rock and Cove Mountain, experienced a nocturnal increase in ozone concentrations which could only be attributable to regional transport in the RL.

6.1 Procedure

The sudden increase in daily maximums over four days from 39 ppb to 48 ppb, to 101 ppb, to 111 ppb at the Nances Grove Monitoring Station was very apparent. In order to better understand the event, several different graphs were made. One was of the high pressure trajectory as shown in figure 6-1, which was also included in the results for section 4.0 and appendix A. Another was to compare graphs of the ozone data of the five Knoxville monitoring stations: Freels Bend, Nances Grove, East Knox Elementary, Spring Hill Elementary, and Alcoa Highway as shown in figure 6-2. A third compares

High Pressure Air Mass Impacting Air Quality in Knoxville
Seven Day Trajectory Ending May 11, 1992



Source: NOAA Daily Weather Maps

Figure 6-1. Trajectory of a High Pressure Airmass Impacting Knoxville, May 10-12, 1992

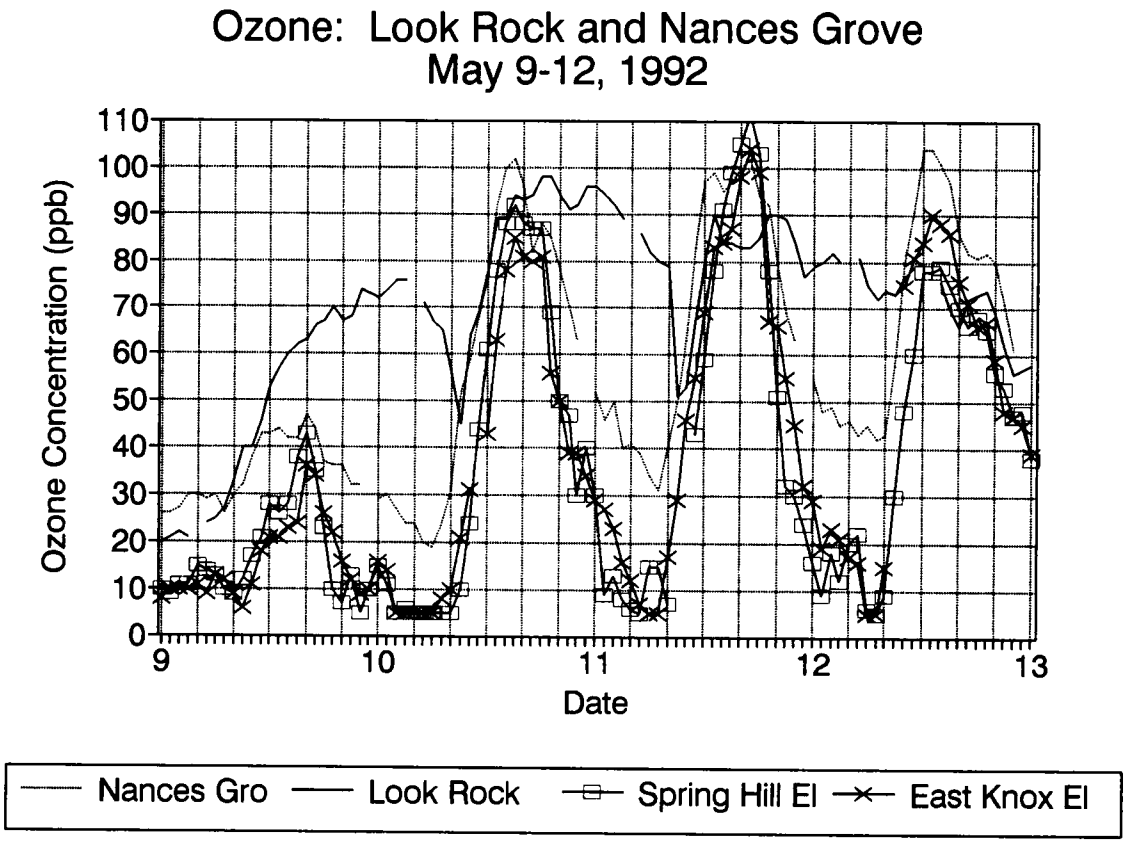


Figure 6-2. Ozone Concentrations around Knoxville, May 9-12, 1992.

data from Look Rock and Nances Grove in figure 6-3. Meanwhile, figures 6-4 through 6-6 include the solar radiation at Look Rock and vector wind directions and speeds at Look Rock and Alcoa Highway.

Ozone Data for Freels Bend and Nances Grove came from the authors files after it passed data quality assurance tests for sites operated for the State of Tennessee as the author was the operator of the stations a that time. All data from Alcoa Highway came from preliminary data provided by the site operator, Mr. Jan Benjamin. Data from Cove Mountain and from Look Rock, but excluding ozone data from Look Rock, came from preliminary data provided by the National Park Service. All other ozone data, including Look Rock, were downloaded from AIRS.

6.2 Proof of Transport in the Residual Layer

Low pressure systems and frontal systems dominated East Tennessee from May 4 through May 9 while ozone concentrations remained quite low, generally less than 50 ppb. As figure 6-1 illustrates, a high pressure system originated in Canada about May 4, and then moved south for two days through the Midwest down to Louisiana. On May 7 the system provided sunny, hot weather for an "L" shaped area extending from Louisiana to Chicago to Maine. On May 8, a low pressure system moved from Western North Carolina to Ohio and split the high pressure

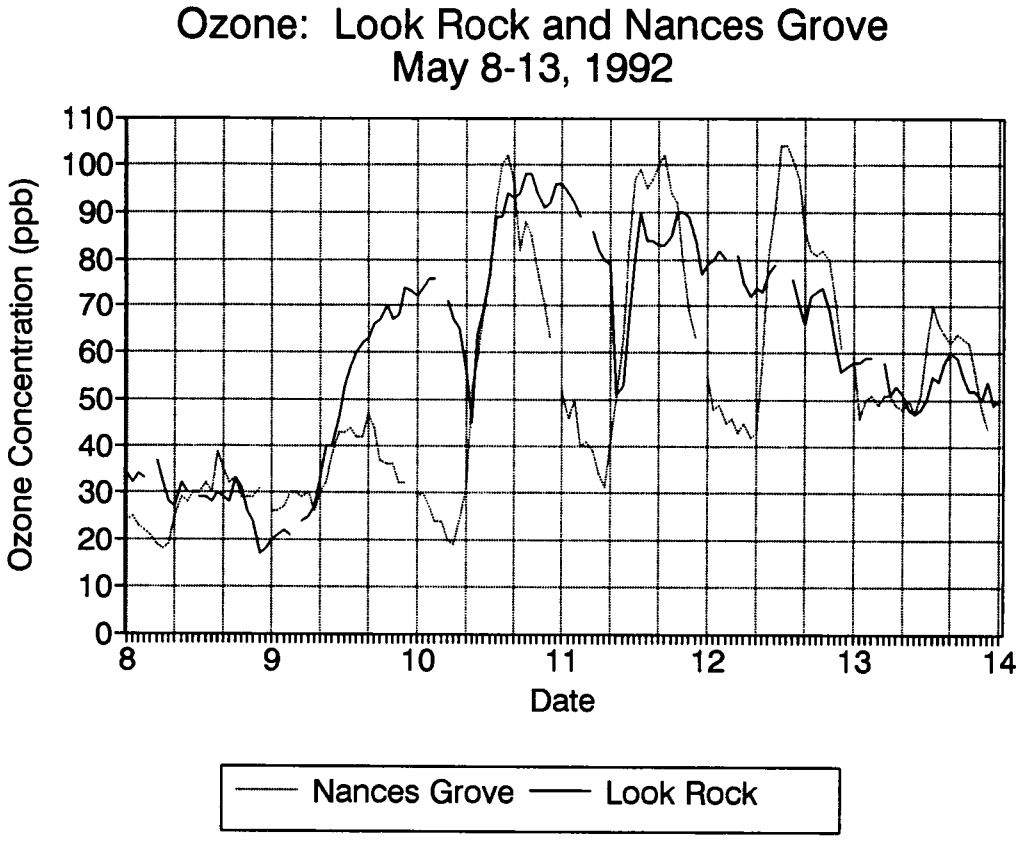


Figure 6-3. Ozone Concentrations at Nances Grove and Look Rock, May 8-13, 1992.

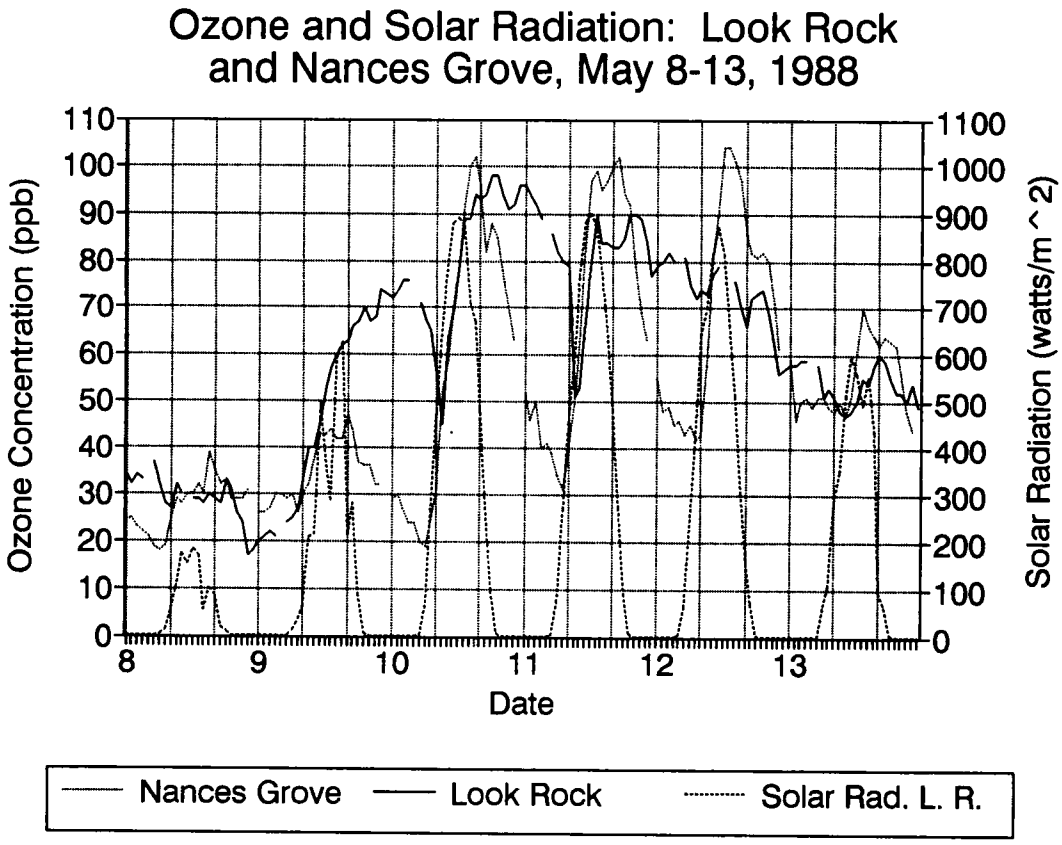
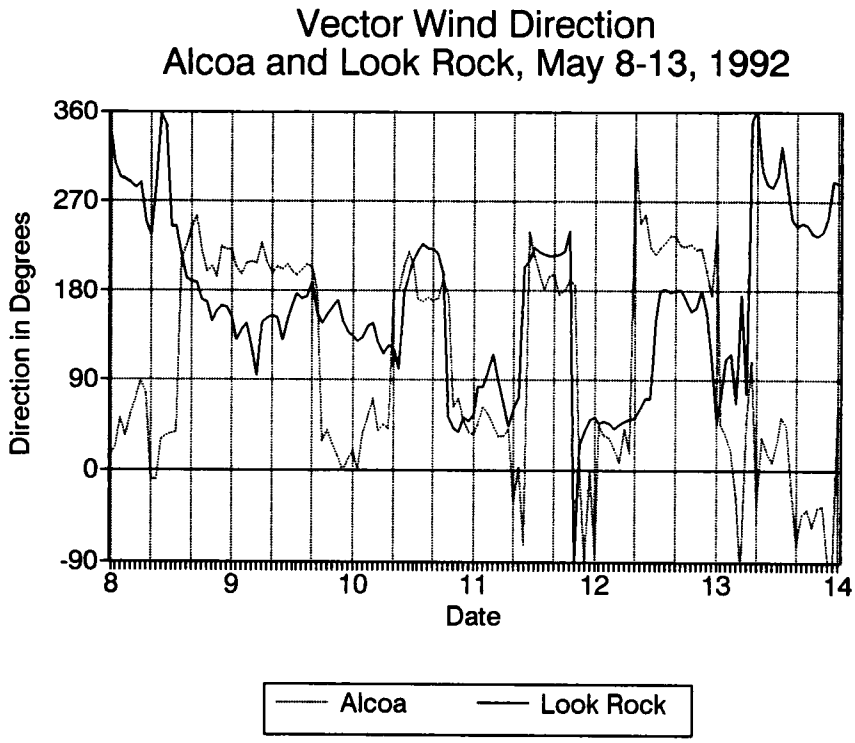


Figure 6-4. Ozone Concentrations at Look Rock and Nances Grove with Solar Radiation at Look Rock, May 8-13, 1992.



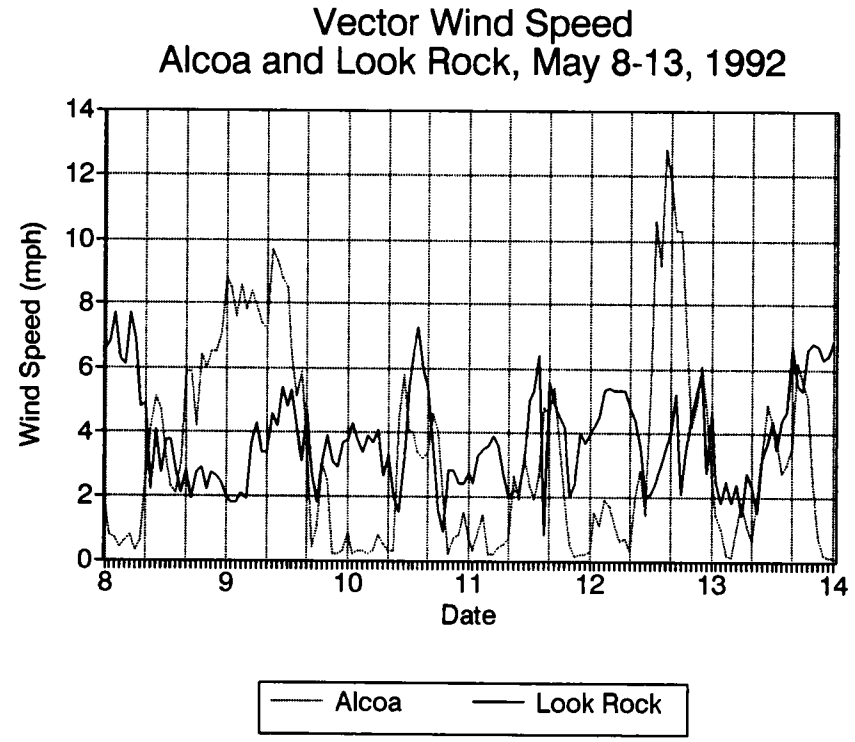


Figure 6-5. A Comparison of Vector Wind Directions and Wind Speeds at Look Rock and Alcoa Highway.

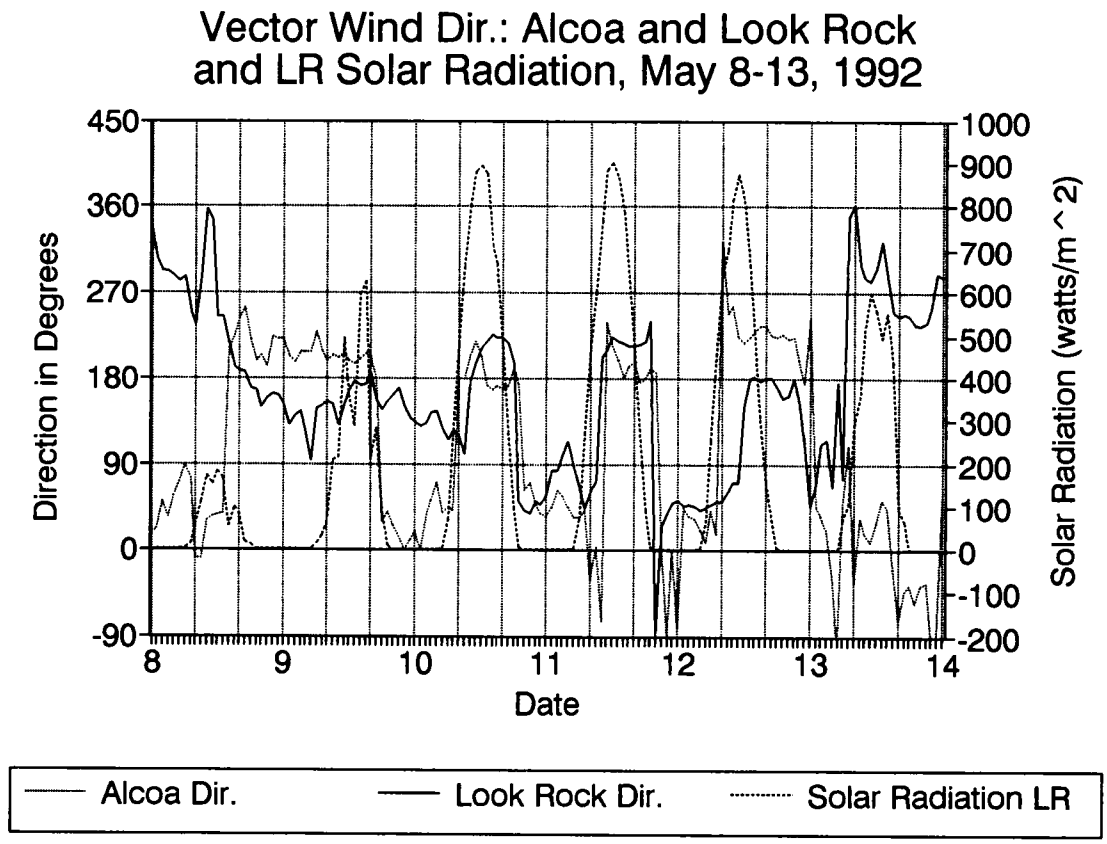


Figure 6-6. A comparison of Solar Radiation at Look Rock and Vector Winds at Look Rock and Alcoa Highway.

system into two pieces. Then, over the next five days the western portion of the high pressure air mass, with the highest barometric reading in the gulf states, moved to the east. The leading edge of this air mass reached East Tennessee sometime between 7:00 am May 9, and 7:00 am May 10.

As figure 6-2 illustrates, ozone concentrations from May 8-13, around Knoxville Tennessee are fairly homogeneous. With the exception of nocturnal observations at Nances Grove, all of the curves have a similar shape with no strong deviations. The total spread of concentrations, again excluding nocturnal stations at Nances Grove, is generally less than 20 or 30 ppb. These similarities between stations indicates that there are no strong plumes from point sources or cities impacting these stations. More importantly all of the SBL stations reported similar values, indicating homogeneity of the air mass.

Although figures 6-1 and 6-2 demonstrate fairly commonplace occurrences, figure 6-3 reveals an interesting example of a nocturnal increase in ozone concentrations at Look Rock on May 9. The same increase was observed simultaneously at Cove Mountain. Since there can be no photochemistry to form ozone at night, such a data trend at two separate stations must either be simultaneous equipment malfunctions or regional transport. However, it would be odd for two separate ozone instruments separated by more than 10 miles of rugged terrain to simultaneously experience the same type of equipment failure. On the other hand, there does

exist the possibilities that the nocturnal increase in ozone could come from sources surrounding the Great Smoky Mountain National Park or from a large concentration in the RL.

Nevertheless there are several considerations that together rule out the possibility that the nocturnal increase in ozone was the result of sources near the Great Smoky Mountains National Park. First of all, the ridges east of these two stations are at least 1,000 to 2,000 feet higher in elevation and would block local sources east of the Tennessee state line in North Carolina. The most probable sources west or north of these stations include Knoxville and several large boilers; but as previously noted in discussions of figure 6-2, there is no evidence of any strong plumes around Knoxville. More convincing evidence lies in the meteorology. As noted earlier, a low pressure system in Ohio had brought clouds and rain to the area surrounding the Smoky Mountains. Notice that, according to figure 6-4, East Tennessee experienced less than 200 watts/m^2 of maximum solar radiation on May 8 and less than 650 watts/m^2 maximum on May 9. In contrast, the area received more than 900 watts/m^2 for three consecutive hours each day for the cloudless days of May 10 and 11. This data then shows cloud cover must have been present on May 8 and May 9, but not for May 10 and 11. With such low amounts of solar radiation, the ozone precursors emitted by sources near Look Rock and Cove Mountain could not have generated significant

amounts of ozone. Therefore, this nocturnal increase in ozone did not originate in East Tennessee or Western North Carolina.

Since the only stations to observe this nocturnal increase in ozone are also the only ones that often lie in the RL, transport in the RL is suggested as the most probable route for the regional transport of ozone during the night of May 9. Clear skies are important in the formation of the SBL since cloud cover prevents the loss of heat that creates the ground surface temperature inversion that creates the SBL and leaves the RL above. Notice that figure 6-4 shows a late afternoon increase in solar radiation on May 9 at 17:00 at Look Rock to almost 300 watts/m^2. This value is much higher than those observed on May 8 and May 13 but is the same as the value observed on the cloudless days of May 10-12. Furthermore, judging by the amount of solar radiation the following morning, all clouds moved out of the area by the sunrise on May 10. As mentioned earlier, May 9 is the same date that the high pressure air mass began to impact East Tennessee. Thus it seems probable that skies in East Tennessee began clearing before sunset on May 9 allowing the SBL and RL to form as a new air mass moved into East Tennessee.

Evidence of the existence of the SBL lies in the regions topography and in the vector wind speed and directions graphed in figures 6-5 and 6-6. Average elevation above sea level decreases in the Great Valley from Bristol through Knoxville

to Chattanooga. This change also occurs in most of the small valleys between the ridges in the Great Valley and becomes important during the formation of the SBL in which air at the ground surface in valleys is no longer influenced by the geostrophic winds of major weather fronts and systems. Instead gravity pulls the coldest air downhill creating a valley wind in East Tennessee of a few miles per hour from the northeast. Therefore, it is not coincidental that at around 18:00 the winds at the Alcoa Highway station suddenly shift to a northeast wind and travel less than 3 miles per hour. Although Look Rock is on a ridge lying on a northeast/southwest axis, there is no observed sudden change in its vector wind direction or speed. The following morning one can again observe a sudden change in wind direction and speed at the Alcoa station that would coincide with the break up of the SBL. In contrast, winds at Look Rock consistently blow from the east to south until after 11:00 at Look Rock. Furthermore, wind directions at the two stations are from similar directions before and after the existence of the SBL at the Alcoa Highway station. As documented in table 6-1 and figures 6-5 and 6-6 this valley wind at the Alcoa Highway station is a fairly consistent phenomena that follows the solar radiation patterns during this ozone episode.

Thus, under the influence of a SBL, the Alcoa Highway station observes an air mass from East Tennessee that is trapped under the RL throughout the night. Its concentration

Table 6-1. Evidence at the Alcoa Highway and Look Rock Stations of the Existence of a Valley Wind.

Date	Morning Changes				Evening Changes		
	Solar Rad. Hour	Wind Dir. Hour	Wind Speed Hour	Ozone Hour	Solar Rad. Hour	Wind Dir. Hour	Wind Speed Hour
8		NA				NA	NA
9	9:00	NA	NA	11:00	18:00	18:00	17:00
10	7:00	8:00	10:00	9:00	18:00	20:00	20:00
11	7:00	8:00	9:00	8:00	18:00	1:00 am on 5/12	20:00
12	7:00	8:00	9:00	8:00	17:00	NA	NA
13	8:00	NA	NA	9:00	16:00	NA	NA

Notes:

"Solar Radiation Hour" is hour solar radiation exceeds or falls below 200 watts/m^2

"Wind Dir..." and "Wind Speed Hour" refers to a change to or from the nocturnal down valley wind direction and speed.

"Ozone Hour" is hour that the ozone concentration at all stations around knoxville exceed 20 ppb.

falls as more and more of this air mass's ozone is deposited to the ground and scavenged near the ground. Meanwhile, lying in the RL, the Look Rock Station is being impacted by the ozone rich air mass moving into the area. Interestingly the full impact of these circumstances is not apparent until the morning of May 10.

6.3 The Impact of the Residual Layer on Stable Layer Ozone Stations after Sunrise

As the earth receives more solar radiation, the ground warms, and the atmosphere forms a shallow ML next to the ground. As the ML grows upward it entrains air aloft which may lie in a SBL, a RL, a capping inversion, or the free atmosphere. In theory, the mixing process distributes pollution evenly throughout the ML. Thus, pollution in a volume of air at an altitude "x" feet above sea level just being entrained will instantly be spread throughout the ML. If this aloft volume of air has lower pollution concentrations than those in the ML, then its entrainment would decrease the pollution concentration in the ML and simultaneously increase pollutant levels where the parcel originated at "x" feet above sea level.

An example of this pollution exchange occurs in the ozone data presented in figures 6-3 and figure 6-4. On May 10, Look Rock lies in the RL at about 2700 feet above mean sea level. As indicated by the accompanying increase in ozone

concentration that occurs as the amount of solar radiation increase, the ML begins to develop around 7:00 am. By 8:00 am the ML is strong enough to reverse the valley wind direction. It is also tall enough to entrain and then mix air at an altitude of 2700 feet as evidenced by the strong decrease in ozone concentrations at Look Rock, which is at elevation 2700 ft. Ozone concentrations continue to decrease during the 10:00 am hour at Look Rock. However, at this important transitional hour concentrations at Look Rock and the SBL stations are roughly equivalent. For the next three hours concentrations increase at the same rate at all of the SBL stations and Look Rock. This change in ozone concentrations at Look Rock is evidence that it now lies completely within the ML. Preliminary data provided by the National Park Service from Cove Mountain, at 4000 feet above mean sea level, indicates that it had higher concentrations of ozone than Look Rock. Thus, it is evident that much of the increase in ozone concentrations during the next few hours is the result of the entrainment of more air with even higher ozone concentrations further aloft.

Although there is no other example of increasing nocturnal ozone concentrations during this episode, the pattern of a drop in concentrations at Look Rock and simultaneous rise in concentrations at Nances Grove is also repeated on May 11, but not on May 12 or 13. These results are summarized in table 6-2. On May 12, Nances Grove and Look

Table 6-2. Parameters of the Drop in Ozone Concentration at Look Rock Due to Vertical Mixing.

Date	Solar Rad. Hour	Wind Change Hours	Ozone Hour	Look Rock Hours	Look Rock Conc.	Conc. Diff.	Conc. Drop
8		NA		NA	19 ppb	o ppb	NA
9	9:00	NA	11:00	NA	25 ppb	-5 ppb	NA
10	7:00	8:00 10:00	9:00	8:00, 9:00	65 ppb	40 ppb	20 ppb
11	7:00	8:00 9:00	8:00	9:00	80 ppb	40 ppb	30 ppb
12	7:00	8:00 9:00	8:00	NA	72 ppb	30 ppb	NA
13	8:00	NA	9:00	NA	53 ppb	3 ppb	NA

Notes:

"Solar Radiation Hour" is hour solar radiation exceeds or falls below 200 watts/m^2

"Wind Change Hours" refers to the hours for which wind at the Alcoa Highway station changed its direction and speed from a valley wind to mixed layer winds.

"Ozone Hour" is hour that the ozone concentration at all stable layer stations around knoxville exceed 20 ppb.

"Look Rock Hours" are the hours that a strong decrease in ozone concentrations is observed at Look Rock due to vertical mixing with the new mixed layer.

"Look Rock Conc." is the ozone concentration at 7:00 am at Look Rock.

"Conc. Diff." is the difference in concentration at 7:00 am between Look Rock and Nances Grove.

"Conc. Drop" is the amount of drop in concentration at Look Rock due to vertical mixing.

Rock have very different concentrations during the early daylight hours; but there is no valley wind flow at the Alcoa Station and the amount of morning solar radiation is low compared to the other dates. Thus, there may not have been strong mixing or a strong vertical gradient of ozone concentrations on May 12 at Look Rock. However, on May 13 both Nances Grove and Look Rock have equivalent concentrations during the early daylight hours, which obscures the evidence of ozone mixing.

Another observation in Table 6-2 is the ozone concentration at Look Rock at 7:00 am in the morning. Generally this time is just before vertical mixing entrains large quantities of air from this altitude. The average concentration at this time of day for May 10 through May 13 is 67.5 ppb, or 0.0675 ppm. Since this concentration is entrained into the ML it represents a contribution of ozone that is separate from that which will be photo-chemically produced. Considering that the RL is much thicker than the SBL and since the ozone concentrations are expected to be constant throughout the RL, this layer of the atmosphere is an important source of ozone for the following day's ML.

6.4 Conclusions

Although a monitoring station on a tall ridge top is near a "ground surface," it is often more exposed to the RL of the

upper boundary layer and not the SBL. Thus, unlike other stations on a ground surface, ozone monitoring stations in the RL will not observe nocturnal ozone depletion from deposition or scavenging.

Since the SBL isolates the RL monitors from the general ground surface, the monitors experience the effects of regional transport not experienced by SBL stations. This May episode provides an excellent example of transport of ozone by a new air mass impacting the area beginning on May 9. The following three nights it provides examples of high ozone concentrations being transported within the same air mass for some distance.

Any area contributes biogenic and/or anthropogenic precursors to ozone. The additional ozone created as a result of these emissions is that area's contribution to the background ozone concentration, which should be the average concentration of a vertical slice of the atmosphere upwind of the area in question. Unfortunately, determining an exact average of the vertical ozone profile is difficult unless one has vertical profile data supplied by a special balloon or airplane. Nevertheless, the RL is far deeper than the SBL and does not experience a nocturnal decrease in ozone. Thus, this vertical average is much more likely to be closer to the concentration observed in the RL than that of a ground level station in the SBL. The average background ozone concentration as presented in table 6-2 in the RL for this May

episode is 67.5 ppb. However, the EPA AQS for ozone is only .12 ppm, or 125 ppb. If this RL concentration of 67.5 ppb is used for a background concentration instead of 10 ppb as might be observed at a SBL station, then the area can only contribute an additional 57.5 ppb of ozone before reaching the standard, instead of 115 ppb of ozone. Thus, monitoring stations on high ridge tops may provide valuable data regarding background ozone concentrations.

7.0 JUNE 11-18, 1988; JUNE 21-27, 1988; JULY 4-11, 1988

After examining the results of sections 4 and 5 it seemed appropriate to investigate regional ozone data for other occurrences of long range transport or storage of ozone in the RL and how these factors might have contributed to the background ozone concentration during the highest ozone episodes experienced from 1988 through 1992 in East Tennessee. Thus, three episodes in 1988 with ozone concentrations greater than 130 ppb were chosen for this portion of the study: June 11-18, June 21-27, and July 4-11. Together, these episodes account for 5 of the top 12 days of ozone concentrations in East Tennessee as listed in table 4-1. The analysis for each of these episodes used the high pressure trajectories developed in section 4, intensively compared data from thirteen monitoring stations in Virginia, North Carolina, and East Tennessee, and produced daily isopleth maps of the maximum ozone concentrations in the Southeast.

The July 4-11 episode is of particular interest because the highest ozone concentration recorded in Knox County from 1988 through 1992 of 150 ppb occurred on July 9 while July 8 and July 10 recorded 120 ppb. As a result, all procedures were first tried for this episode and then applied to the other two episodes. Nevertheless, one can find the complete set of graphs for each episode in Appendix B.

7.1 Determining the Land Area to Study and the Specific Stations to Examine Intensively.

In order to determine the background ozone concentration present during high ozone concentration episodes, the area contributing to the background concentrations must be determined. As illustrated in section 4 of this thesis, the specific land masses that a high pressure air mass passes over do not seem to impact the episode's maximum concentration in East Tennessee. However, section 5 demonstrates that an air mass can itself bring with it a high concentration of ozone to an area. Furthermore, the NOAA Daily weather maps show that high pressure air masses can cover many states at one time. Thus, the author decided to examine daily maximum concentrations for June 11-18, June 21-28, and July 4-11 for most of the Southeast, including Alabama, Delaware, Georgia, Kentucky, Maryland, North Carolina, Tennessee, Virginia, West Virginia and the District of Columbia. Mississippi was not included because there were few ozone monitoring stations in that state, and relatively few high pressure air masses that impact East Tennessee travel through that state. Florida was excluded because most of that state is a considerable distance from East Tennessee. All South Carolina data were also excluded since there were many daily maximums reported in the AIRS Raw Data Reports that were higher than the maximum values for the same stations as listed in the Quick Look Reports. Certain stations in Virginia near Washington, D. C. were also

excluded for the same reason. The remaining stations' Raw Data Reports were then downloaded from the EPA AIRS for the months of June and July of 1988.

Using the SAS Mapper program on the University of Tennessee, Knoxville VAX Mainframe, preliminary graphs of the spatial distribution of ozone daily maximum concentrations for each day for July 4-11 were made. It was then observed that the high pressure system for this episode moved Southwest from Maine and then stalled for several days just northeast of the Cumberland Gap where Tennessee, Kentucky, and Virginia meet. Likewise, high ozone concentrations seemed to move down the Shenandoah Valley into Southwestern Virginia then into East Tennessee. Based on these observations a collection of SBL and RL stations were chosen for more intensive analysis. Starting near the northeastern end of the Shenandoah Valley and moving southwest, the RL stations are Dickey Ridge, Max Meadows, Saw Mill Run and White Top Mountain. Likewise the SBL stations were in Fauquier County, Roanoke, and Marion, Knox County, and Hamilton County. Figure 5-1 is repeated as figure 7-1 and shows the relative location of these stations.

Unfortunately, several stations examined in section 6 of this thesis were not available for these three episodes. Cove Mountain and Look Rock data were not available on AIRS for most of June and July of 1988; and the Nances Grove, Freels Bend, and Alcoa Highway stations were not in operation before 1990.

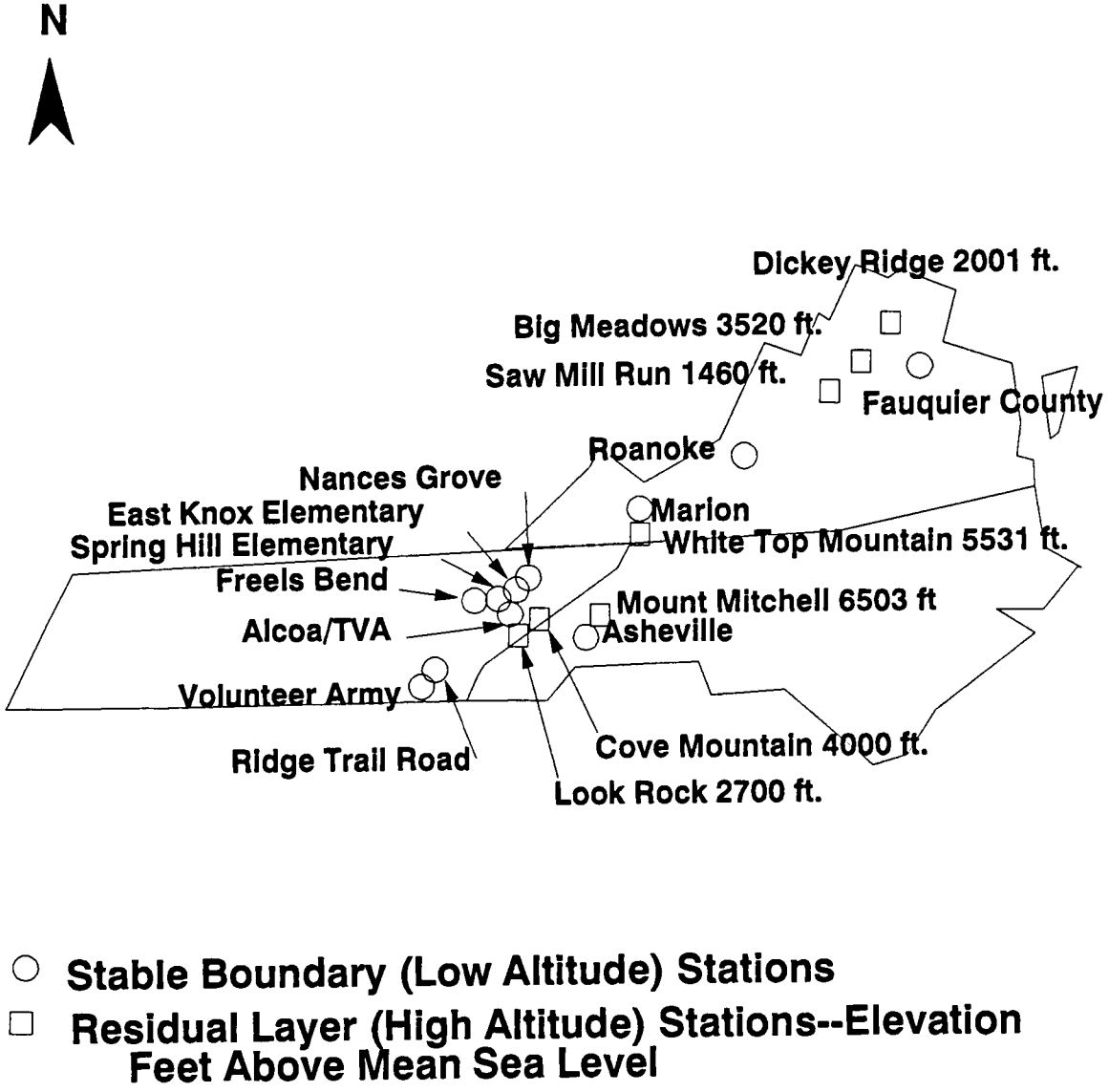


Figure 7-1. Ozone Monitoring Stations Intensely Studied; Figure 5-1 Repeated for Convenience.

After some study of the effect of elevation on ozone concentrations during the July episode, two more stations in North Carolina were added to the intensive study list, Mount Mitchell and Asheville. The State of North Carolina supplied the Mount Mitchell Data and the Asheville Data were available on AIRS.

7.2 Developing the Eleven Hour Dampened Ozone Concentrations

After selecting an area to study and specific stations to study, a procedure to compare observations at the selected stations was developed. The first step was to make graphs showing various combinations of stations. One of the first observations was that the stations on exposed ridge tops did not experience a diurnal cycle for ozone concentrations, but a seven or eight day cycle. However, one of the more striking observations was that daily maximum concentrations at SBL stations appeared in several cases to be nearly equal to the simultaneous concentrations observed at the nearest RL station.

It is important to remember, that the strong decrease in ozone concentrations of SBL stations is associated with onset of atmospheric stability as the SBL grows to an altitude that includes that station. This stability prevents ozone aloft from mixing down to replace ozone lost to NO_x scavenging or ground surface deposition. Consequently, stations on valley

floors experience a strong decrease in concentrations very near sunset while stations on low ridges may not experience a drop until nearly sunrise. As long as any station lies in the RL above this SBL it will not observe the same cause and effect decrease in ozone concentrations. However, stations that still lie just above the SBL near sunrise can still observe a decrease in ozone as the growing ML entrains ozone rich air aloft into ozone depleted air below. As a result, this mixing increases concentrations at the SBL station and decreases concentrations near the affected RL stations. After some time such a RL station is completely incorporated into the ML. Therefore, there should be little difference between it and a nearby lower altitude station until the next SBL forms.

Consequently, as one rises in altitude the less impact the SBL has and the more stable ozone concentrations are. In turn this implies, that at some altitude concentrations will be relatively stable throughout the day and that the dominating factors that determine ozone concentrations should be where the air parcel has traveled and when it made its journey, which in turn dictates mixing heights, the amount of solar radiation, and the various anthropogenic and biogenic emissions to which the air parcel has been exposed. Since these parameters are quite variable from place to place, ozone at high altitude RL stations should be expected to have many small variances that overlay relatively stable concentrations

throughout the day. Borrowing terminology from electrical communications theory, the author of this thesis compares these small peaks and valleys to "noise" concentrations associated with atmospheric eddy currents and ozone enriching and ozone depleting plumes that "modulated" or covered an average regional background concentration, or "carrier signal."

Therefore, a systematic trial and error graphing approach was used to dampen this noise characteristic for these episodes. The first trial began by averaging the current hour, one hour before the current hour, and one hour after the current hour. This scenario would be called a "three hour dampened concentration," or "moving average." If needed, successive trials would add one hour forward and one hour backward to the overall average. Thus, the dampening time would always be an odd number so that it will include the current hour and not forecast or remember ozone concentrations. One of the criteria established for stopping the iterative process required that the dampened data average any two successive maximums and minimums. Another was that the averaging time not be so long that important changes in ozone, concentrations, from a new incoming air mass for example, were stifled. After trying several different averaging times, the eleven hour averaging time was chosen as the dampening time. Located in National Parks and National Forests, the RL stations in the intensive study list

are isolated from large point sources. Since rural areas only contribute a small amount of ozone, the concentrations observed at the RL stations must be dominated by regional transport, not photochemistry. Thus, the eleven hour average clearly shows the general trend in ozone data at these stations due to a small amount of photochemistry and due to regional transport in the day or night. Since the additional ozone actually produced in rural areas is expected to be quite small compared to urban areas, then the 11 hour dampened plot should track changes in the background concentration due to regional transport from the urban areas nearest these stations.

To test these ideas and show the impact of the RL on local ozone concentrations, these eleven hour averages were compared to curves from nearby SBL stations and then also to a larger metropolitan area such as Knoxville, Roanoke, or Fauquier County Virginia (just outside the suburbs of Washington D. C.) Tables were then created to quantify the absolute difference between the RL eleven hour average and the SBL station observation at the time of the maximum for the SBL station. Since the upper air stations have such small variances over several hours as compared to other stations, a small difference would show that ozone in the RL is the primary influence on concentrations at the ground surface. A large difference of 40-50 ppb would indicate that the relationship between the two layers is weak. Keeping track of

the signs could prejudice the results by averaging out large positive and negative differences that would otherwise indicate that the RL has a weak impact on ground level ozone concentrations. These tables are quite revealing since the differences were often less than expected.

7.3 Developing the Ozone Isopleth Maps

At this time the analysis of these episodes returned to the ozone isopleth maps. These graphs were examined to determine if they supported conclusions concerning the RL and the role of high pressure air masses to bring high background concentrations with them to an area. First a large data file of AIRS Raw Data Reports was constructed. Each raw data file is for one station for one month with the days of the month on separate rows and the hours of the day in columns with the last column being the daily maximum ozone concentration. The SAS software read the regional ozone data file and extracted the daily maximum ozone concentration and converted each station's latitude and longitude into its own coordinate system. For each day SAS created a separate ASCII output file that consisted of the station's x and y coordinates and the maximum ozone concentration for that day. If the station was in the regional raw data file for any part of a month, then SAS output a maximum value for that station for any date in that month. Therefore, this output file was edited for zero

concentrations, concentrations that were low enough that one could question if the monitor operated the entire day, and concentrations that were higher than typically found in the AIRS Quick Look Reports. A single separate run created the coordinates to draw state boundaries. The Surface3 program used the SAS output and the state boundary file to plot the station locations, derive and plot the contours, and draw state boundaries.

To create the contours, Surface3 divides the graphing area into a grid in x and y coordinates with the number of rows and columns specified by the user. As noted in table 7-1, a grid size of 50 by 50 was chosen for this analysis. Then for each grid point for which there is no real data point (ozone concentrations), the program uses the surrounding real data points to determine a z axis height (or ozone concentration). For this application a simple distance weighted average of the nearest ozone monitors was selected. Also an effort was made to include only data from nearby stations. The parameters used in this program are shown in table 7-1.

To show the typical station locations used to create the ozone isopleth maps, the stations from the regional ozone database used on July 9, 1988, were plotted in figure 7-2. Areas represented by three or more stations include Atlanta, Birmingham, Memphis, Nashville, Louisville, Cincinnati, Ashland/Huntington, Washington D.C., Baltimore, Richmond,

Table 7-1. Parameters Used in Surface3 to Creating the Ozone Isopleth Maps.

Parameter Name	Parameter Value
Number of Rows	50
Number of Columns	50
Southwest Corner	-.109 (x), -.089 (y) Generic Distance Units
Northeast Corner	.104 (x) .092 (y) Generic Distance Units
Maximum Distance of Nearest Monitoring Station to Plot a Data Point	.029 Generic Distance Units
Maximum Distance to Any Monitoring Station to Include in Weighted Average	0.04 Generic Distance Units
Distance Weighting Function D=Distance to Real Data Point, Dmax=.04 units	$w=(1-x)^2/x^2$ x=D/(1.1*Dmax)

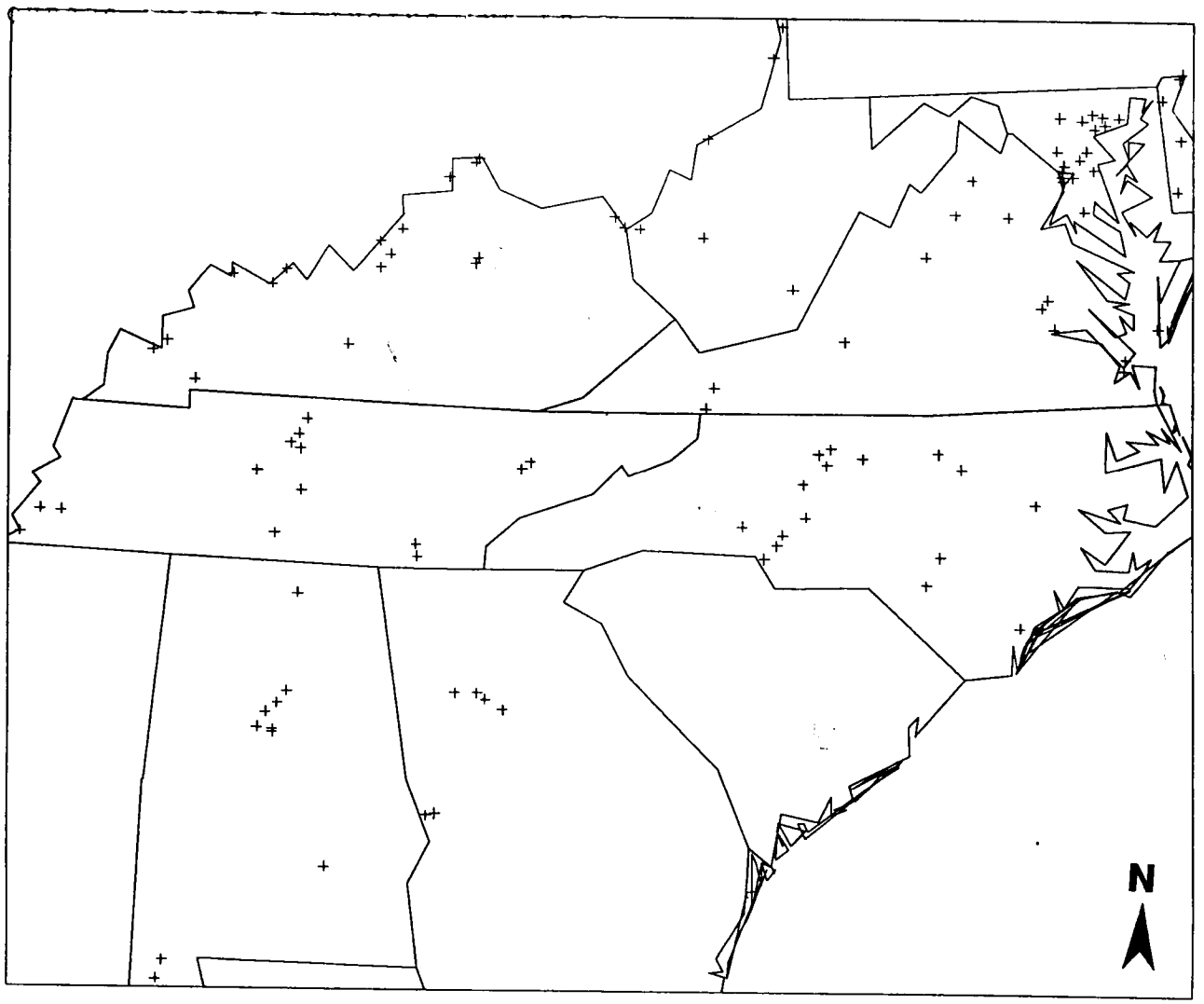


Figure 7-2. Stations Plotted on July 9, 1988, to Create the Ozone Contours.

Charlotte, and the North Carolina Triad. Although many of the stations are near urban areas, there are numerous monitors placed in rural areas well away from urbanization: Forest Service sites in West Virginia and Alabama; National Park Sites in Kentucky, Tennessee and Virginia, and Tennessee Valley Authority sites in Kentucky, Virginia, and Tennessee. As will be demonstrated earlier few of these remote stations show more than 10 or 20 ppb difference between them and nearby areas. In this monitoring network only a few very large urban areas like Atlanta and Washington, appear to be islands of much higher concentrations than their immediate surroundings. Furthermore the areas with largest ozone holes are near urban areas in Kentucky: Ashland, Louisville, and Lexington. These may be the result of high urban NO_x concentrations that would scavenge ozone the same way that NO_x in a power plant plume does. Thus, the comparative scarcity of rural ozone monitors does not seem to inflate ozone concentrations.

7.4 The Results from Eleven Hour Dampening

The results presented in this section apply equally well to all three episodes. Consequently, presenting graphs for each episode would be redundant and make the text quite disjointed. Thus, unless one of the other episodes has a more illustrative or striking example, the examples displayed in

the figures for this section are from the July 4-11, 1988, episode. Nevertheless, a full set of graphs for each episode appears in Appendix B.

As shown in figure 7-3, ozone at higher altitudes like White Top Mountain do not show a strong diurnal pattern. Also the eleven hour dampening average very clearly shows the eight day trend in ozone data as it averages out the ozone enriching and depleting plumes. As shown in figure 7-4, the same basic relationship between hourly concentrations and eleven hour dampening exists in data from Dickey Ridge and Mount Mitchell. At all three of these stations, there is very little, if any, direct influence of the SBL because there is no recurring strong nocturnal or early morning drop in ozone concentrations. Moreover, there are no daily events that cause a peak or valley to reappear the same time each day at any of these stations.

As figure 7-5 shows, ozone data at Saw Mill Run has a recurring decrease which is often near sunrise. As was observed in the Look Rock data for the May episode discussed in section 5, the often sudden decrease in concentrations could be the result of air below with nearly 0 ppb of ozone mixing with the air at Saw Mill Run and decreasing the concentration aloft. However, since the drops in concentration often occur several hours before sunrise it seems more likely that the drop in ozone concentrations is an indication of when the SBL reaches the elevation of Saw Mill

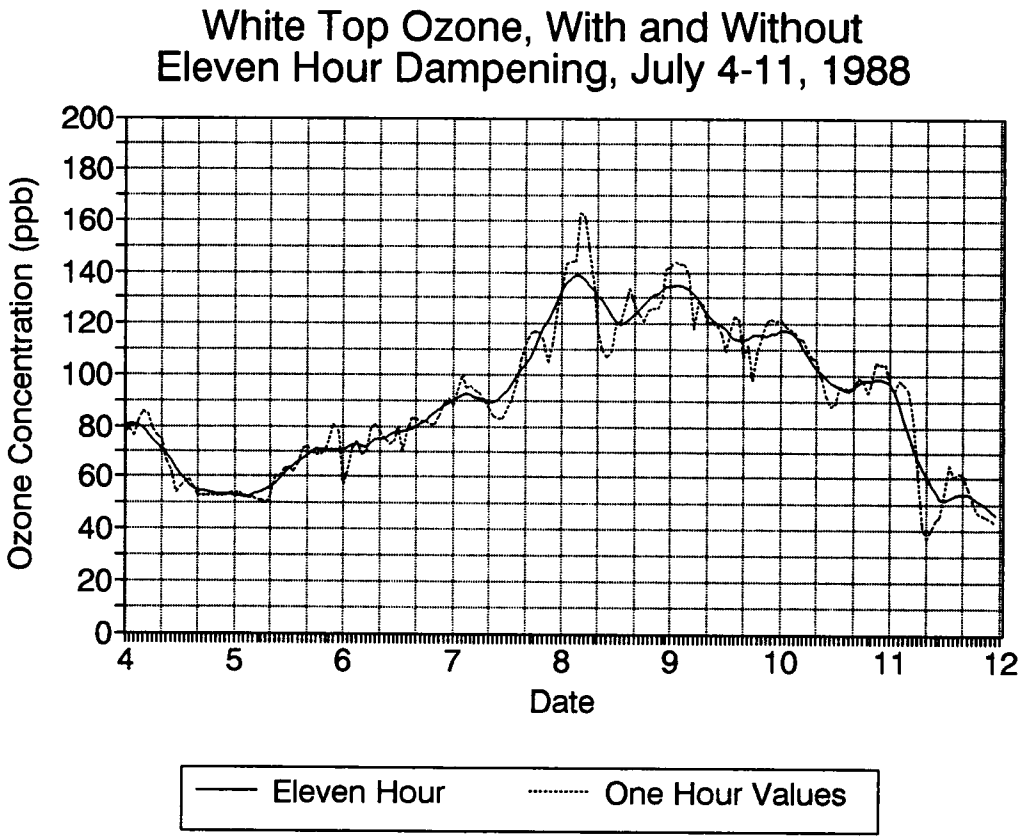
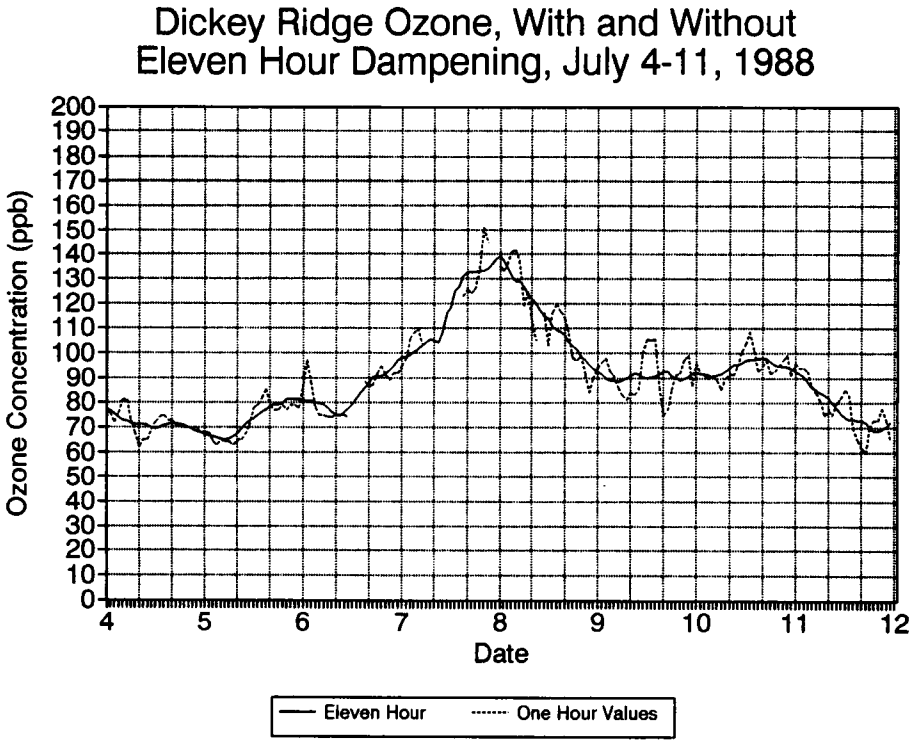


Figure 7-3. A Comparison of Hourly Ozone Concentrations and Eleven Hour Dampening at White Top Mountain July 4-11.



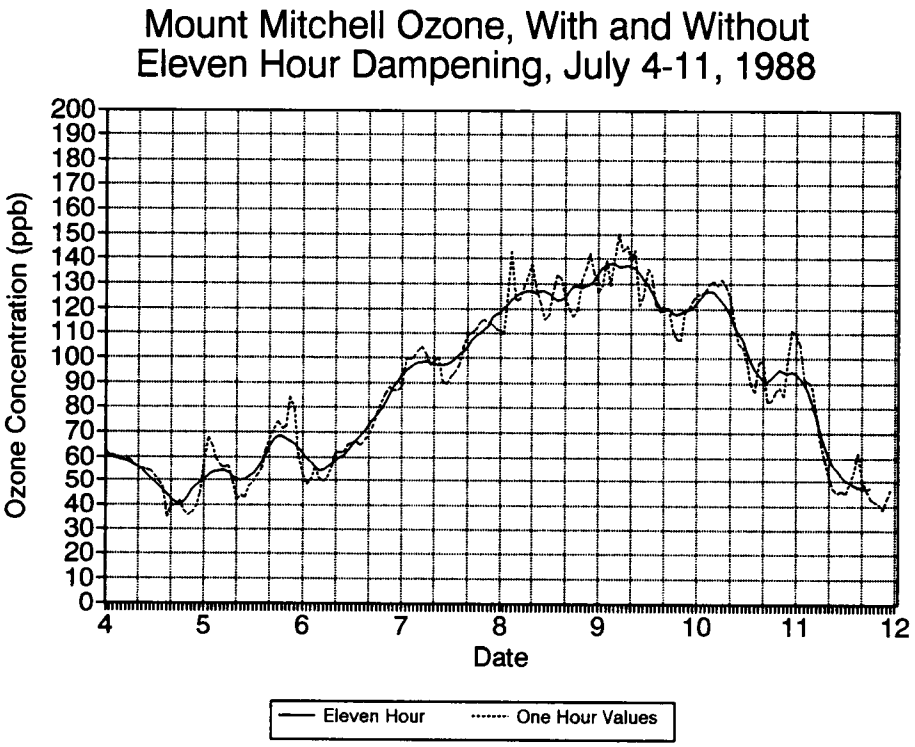


Figure 7-4. Comparisons of Hourly Concentrations and Eleven Hour Dampening at Dickey Ridge and Mount Mitchell for July 4-11.

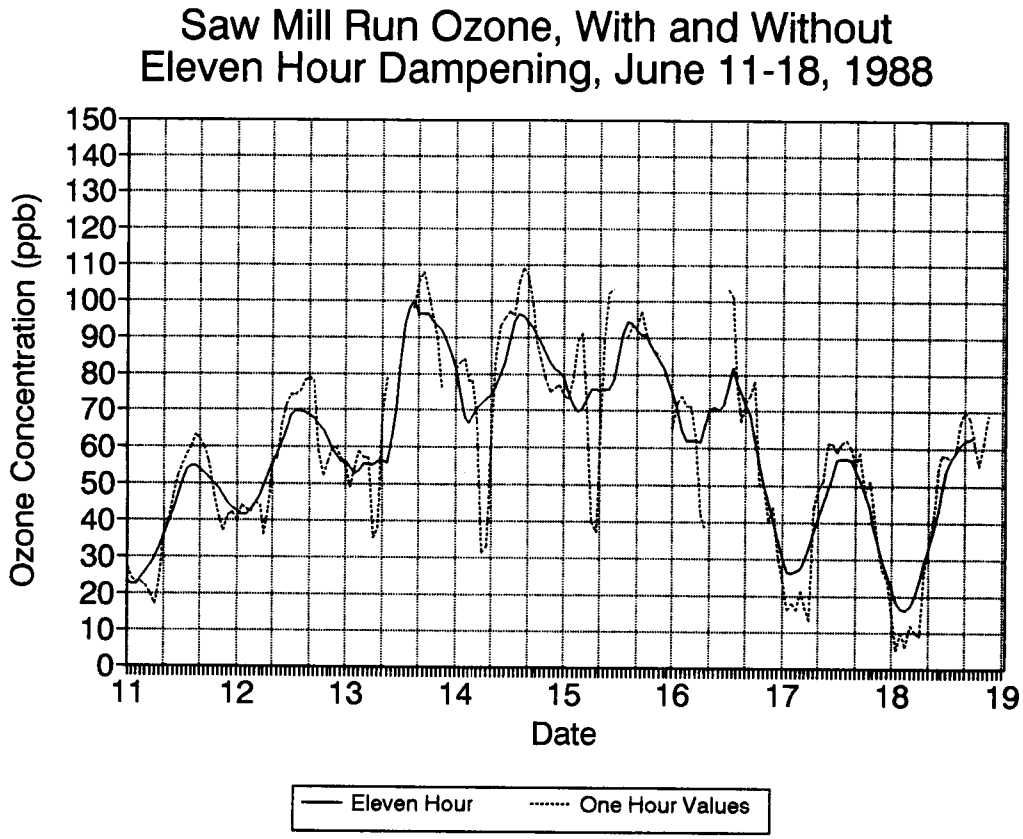


Figure 7-5. A Comparison of Hourly Concentrations and Eleven Hour Dampening at Saw Mill Run for June 11-18.

Run. Since the SBL grows from the ground up, it seems probable that Saw Mill Run is often above this layer for much of the night. Even so, it has such a strong effect that both the hourly averages and the eleven hour averages have diurnal patterns.

Thus, the eleven hour dampening could only help determine a regional background concentration when the SBL does not strongly influence the station directly or indirectly through vertical mixing. This then helps confirm that the peaks and valleys averaged out with eleven hour dampening at stations like White Top Mountain are not the result of atmospheric structure changes, but of ozone enriching and depleting plumes from major point sources and cities. Otherwise the eleven hour averages would also have a diurnal pattern. Thus, an eleven hour average applied to a strong RL station gives an indication of the aloft background concentration for the nearby area. Thus, one could estimate the RL's impact on region-wide ozone concentrations by comparing the local SBL station daily maximums to concurrent eleven hour dampened RL averages. These results are summarized in table 7-2.

One of the most intriguing comparisons is between Marion Virginia and White Top Mountain as shown in figure 7-6. Being in a very rural area, there are few sources near Marion except a rural interstate; consequently, local photo-chemistry should only add small amounts of ozone to the ambient concentration, but on two days the ambient ozone

Table 7-2. The Differences in Concurrent Ozone Concentrations Observed in Eleven Hour Dampened Concentrations at Residual Layer Stations and Daily Maximums at Stable Layer Stations for June 11-18, June 21-28, and July 4-11, 1988.

SBL Station/ RL Station	Date-June 1988								Avg.
	11	12	13	14	15	16	17	18	
Fauquier/Dickey Ridge	4	2	10	20	7	5	25	3	10
Roanoke/Dickey Ridge	5	5	5	12	23	7	35	0	12
Roanoke/Saw Mill Run	7	20	30	17	20	30	23	10	20
Roanoke/White Top	3	20	32	27	30	35	7	5	20
Marion/White Top	5	7	0	3	5	0	0	0	3
Knoxville/White Top	5	30	27	30	50	7	20	10	21
Knoxville/Mount Mitchell	10	30	15	25	40	15	3	5	18
Chattanooga/White Top	10	32	25	30	30	20	37	34	27
Asheville/Mount Mitchell	3	3	3	0	10	3	10	8	5

SBL Station/ RL Station	Date-June 1988							Avg.
	21	22	23	24	25	26	27	
Fauquier/Dickey Ridge	17	15	33	17	10	10	20	15
Roanoke/Dickey Ridge	1	2	22	22	25	30	5	13
Roanoke/Saw Mill Run	29	17	22	10	20	20	7	16
Roanoke/White Top	25	20	18	25	7	18	0	14
Marion/White Top	2	0	6	2	8	12	2	4
Knoxville/White Top	0	45	15	60	17	10	5	19
Knoxville/Mount Mitchell	5	60	10	45	15	10	5	19
Chattanooga/White Top	0	30	12	50	14	5	25	17
Asheville/Mount Mitchell	10	25	1	10	1	0	3	6

SBL Station/ RL Station	Date-July 1988								Avg.
	4	5	6	7	8	9	10	11	
Fauquier/Dickey Ridge	5	10	10	30	20	20	12	30	17
Roanoke/Dickey Ridge	0	6	10	4	10	27	20	16	12
Roanoke/Saw Mill Run	3	10	10	12	12	34	34	30	18
Roanoke/White Top	15	17	19	35	0	0	20	38	18
Marion/White Top	15	3	3	2	1	4	5	8	5
Knoxville/White Top	20	1	12	0	0	35	35	2	13
Knoxville/Mount Mitchell	33	5	20	3	5	30	25	3	16
Chattanooga/White Top	25	20	10	12	20	5	0	0	12
Asheville/Mount Mitchell	10	5	2	0	15	28	5	10	9

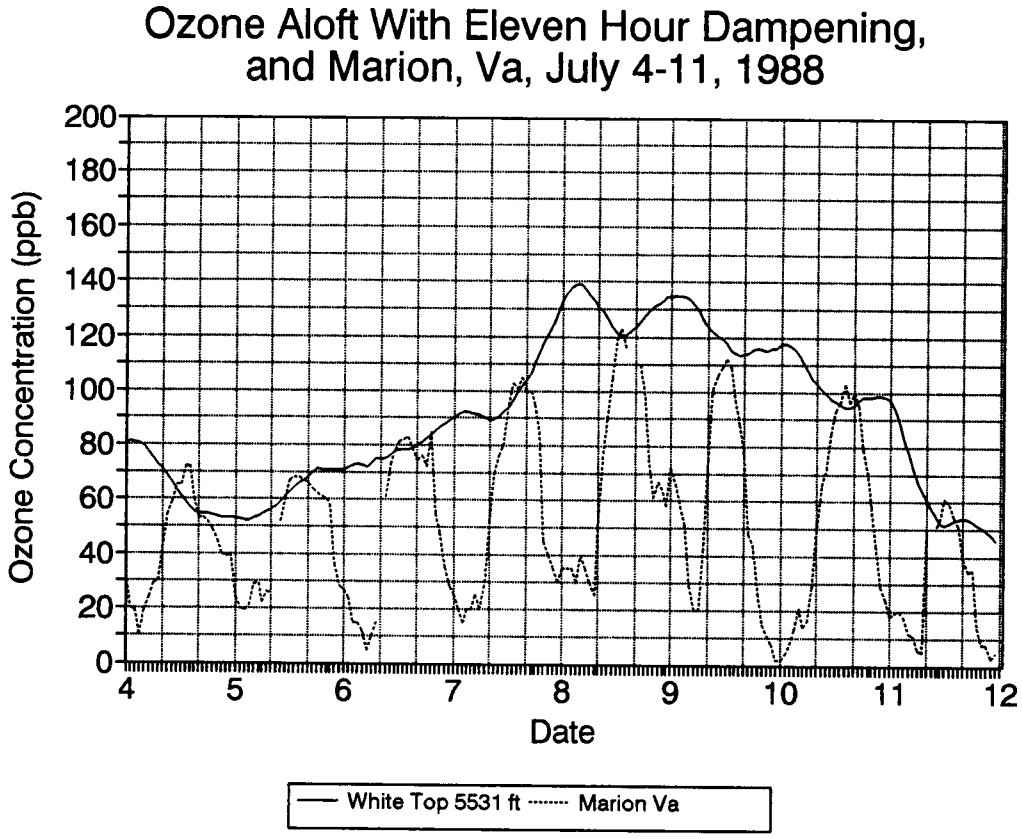
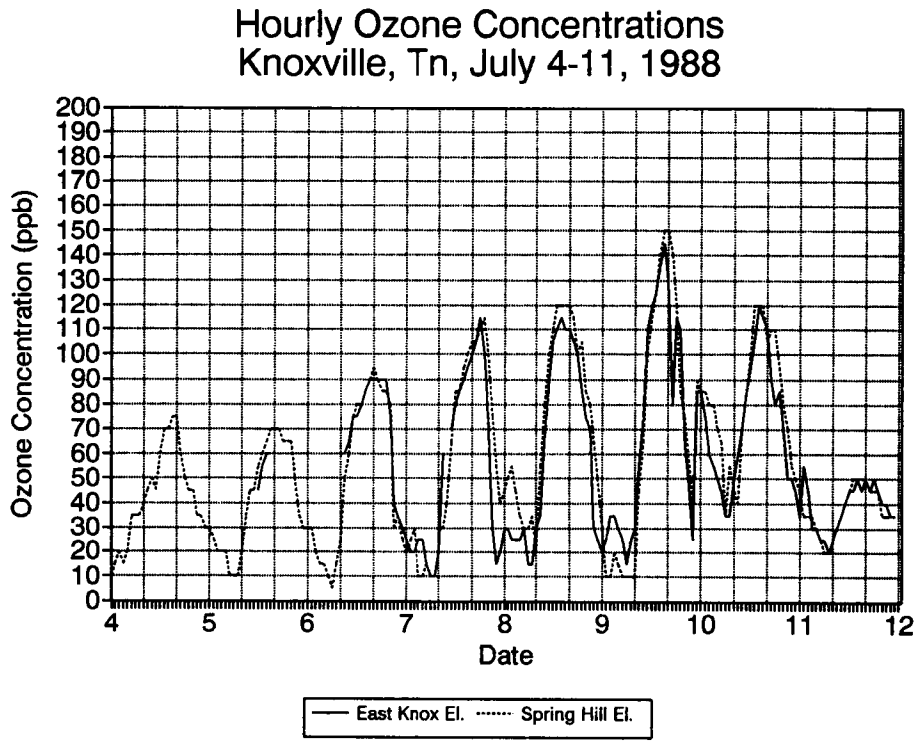


Figure 7-6. A Comparison of 11 Hour Ozone Concentrations at White top Mountain and 1 Hour Concentrations at Marion, Virginia, July 4-11, 1988.

concentrations reach 90 ppb and all but one of the daily maximums for all three episodes are over 60 ppb. Furthermore, the daily maximum concentration at Marion is usually within 5 ppb of the concurrent eleven hour average at White Top. Out of the 23 days in the 3 episodes, there were 14 instances in which the graph of ozone concentrations at Marion were beginning to peak as the dampened concentration on White Top Mountain was decreasing.

Similar results are observed in the comparisons of Asheville and Mount Mitchell where the difference is less than 9 ppb. Also there are fourteen days in which the concentration at Asheville peaks as the 11 hour concentration on Mount Mitchell decreases. As presented in table 7-2, the remaining averages between comparisons of daily maximums and concurrent eleven hour averages varies from 10 ppb to 27 ppb and averages 17 ppb. These results are in spite of including station pairings like Fauquier County/Dickey Ridge and Chattanooga/White Top. In fact if one ignores the Marion and Asheville data and the 27 ppb average difference in concentration between Chattanooga and White Top from June 11-18, 1988, then these average difference only range 11 ppb, from 10 to 21 ppb. In line with these results, the average difference in maximum ozone concentrations around Knoxville and the simultaneous 11 hour dampened values at White Top and Mount Mitchell is 18 ppb.

The numerical similarities just described simply reflect graphical similarities between various groupings of stations. For instance figure 7-7 shows that the difference between the daily maximums at the station pairs around Knoxville and Chattanooga is generally less than 10 and 20 ppb. Notice also that figure 7-8, a comparison of Roanoke and Saw Mill Run data, is very much like the figures in section 5 comparing Nances Grove and Look Rock. Both sets of graphs show that after ozone concentrations at the upper layer station falls dramatically and becomes equivalent to those at the ground level station, both stations observe the same increase in ozone concentrations. The graphs then diverge sometime after the SBL station reaches its afternoon maximum. As shown in figure 7-9 the RL stations also have very similar graphs during these episodes. Although there are some differences in these various graphs, sections 7.5 through 7.7 show that the particular meteorological events at the different stations account for these differences. Another important similarity is that at most SBL stations the daily maximum is greater than the concurrent 11 hour concentration at a RL station. The exceptions are Marion, where ozone levels could be lower or higher than at White Top; Asheville, where concentrations are often lower than Mount Mitchell; Chattanooga, which is consistently lower than White Top only during the July episode; and Roanoke, where concentrations could be higher or lower than the 1 hour concentrations at Saw Mill Run.



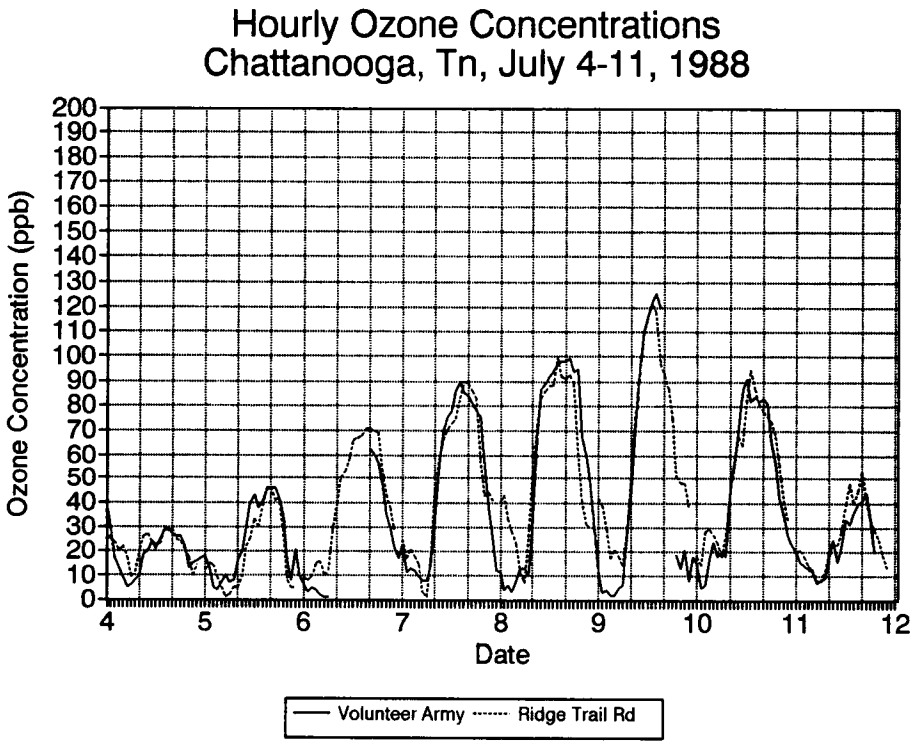


Figure 7-7. A Comparison of Ozone Concentrations around Knoxville and Chattanooga, July 4-11, 1988.

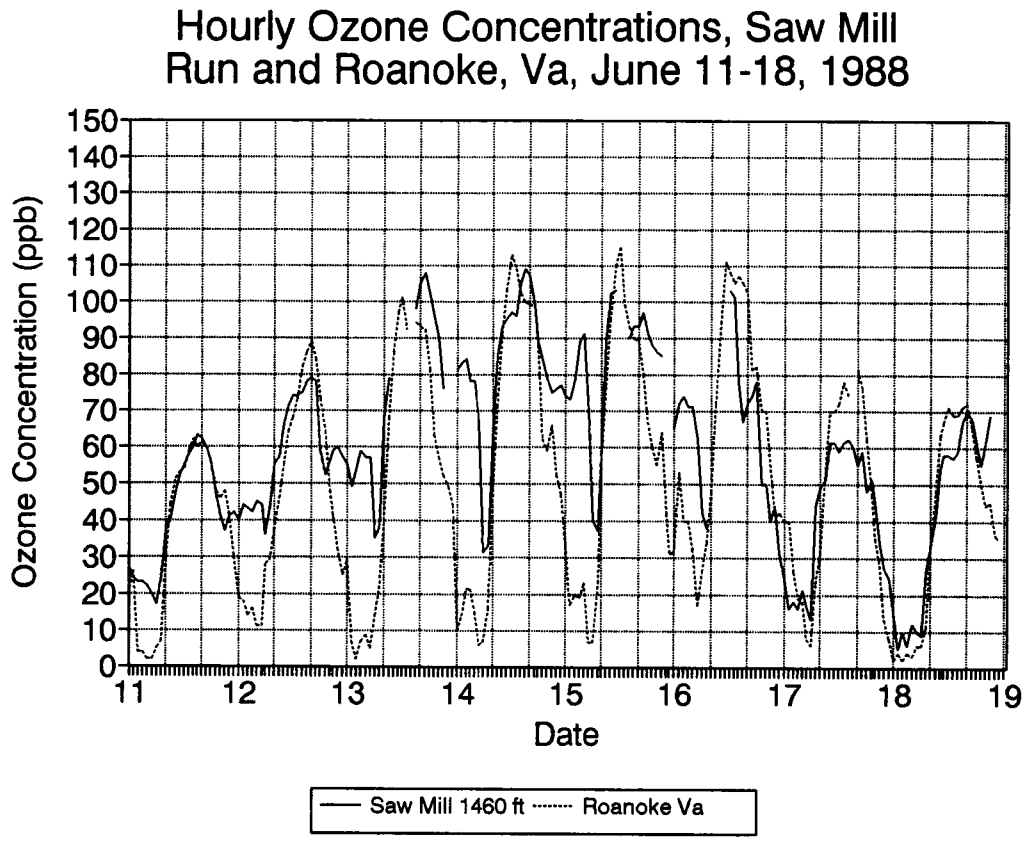
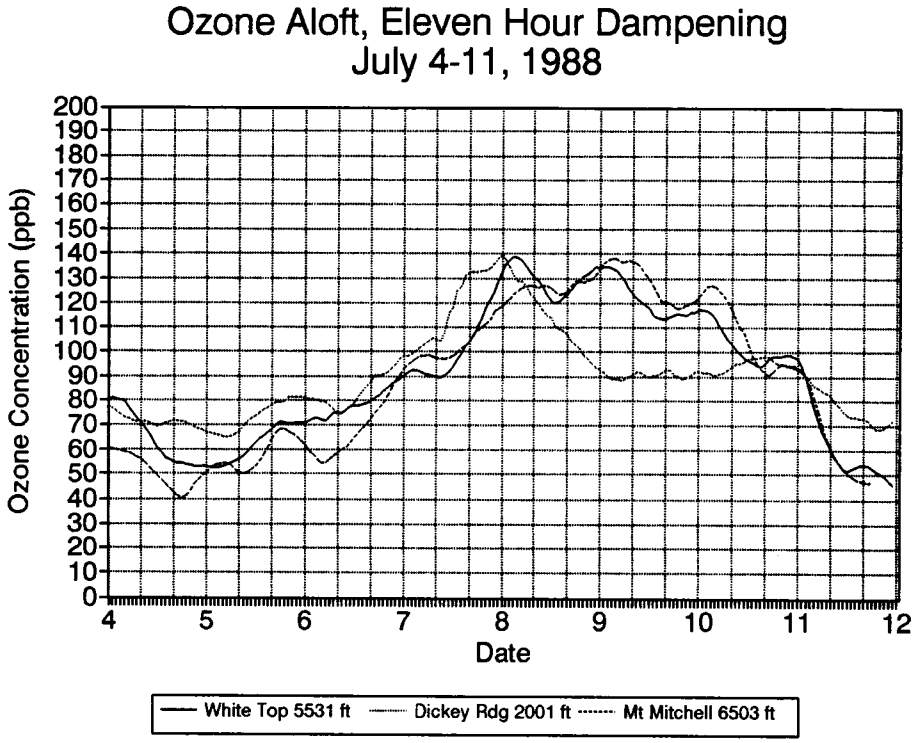


Figure 7-8. A Comparison of Hourly Ozone Concentrations at Saw Mill Run and Roanoke Virginia, June 11-18, 1988.



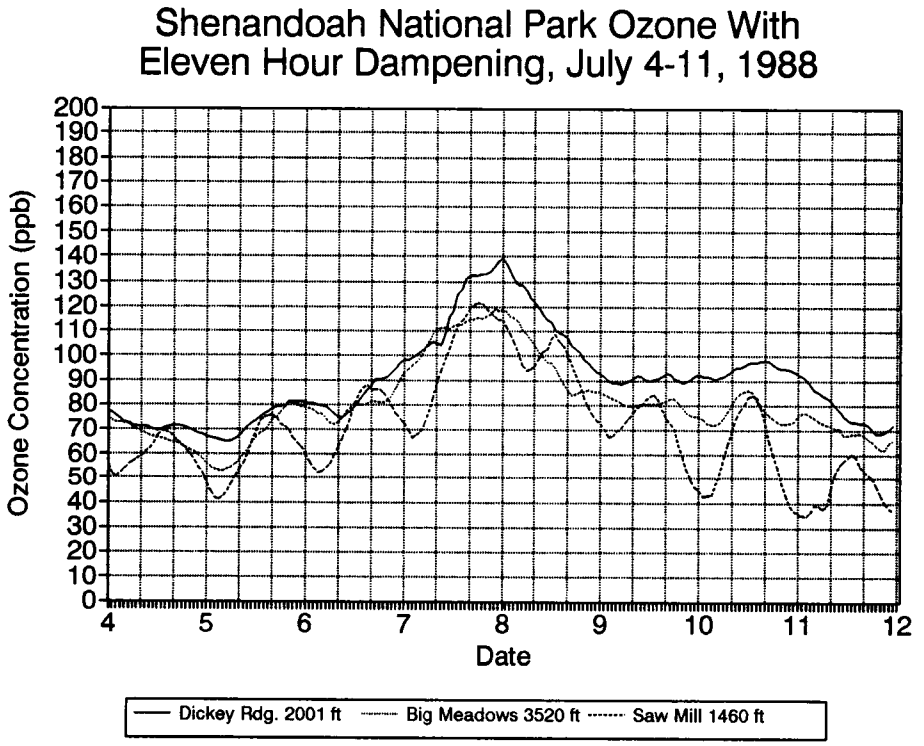


Figure 7-9. A Comparison of 11 Hour Dampened Ozone Concentrations Observed at Residual Layer Stations, July 4-11, 1988.

However, it should be noted that a relationship between ozone at White Top and Chattanooga could be rather tenuous since they are so far apart. Also, Roanoke daily maximums are still usually higher than the simultaneous 11 hour concentrations at Saw Mill Run, Dickey Ridge, and White Top.

7.5 Source of Meteorological Information

The meteorological data used to help analyze similarities and differences in ozone concentrations comes from the "Daily Weather Maps" issued by the NOAA. A sample of a typical daily report is supplied in figure 7-10. One such page is compiled for each day. A week's worth of maps is in one publication. Each page contains a large map of the United States and Southern Canada showing the surface frontal systems, synoptic events, and surface observations: pressure, temperature, and wind direction and speed. There is also a chart of the 500 millibar height contours and winds. All data collected for these two maps represents data collected at 7:00 am that day. The other two smaller maps show the maximum and minimum temperatures and areas of rainfall for the previous day.

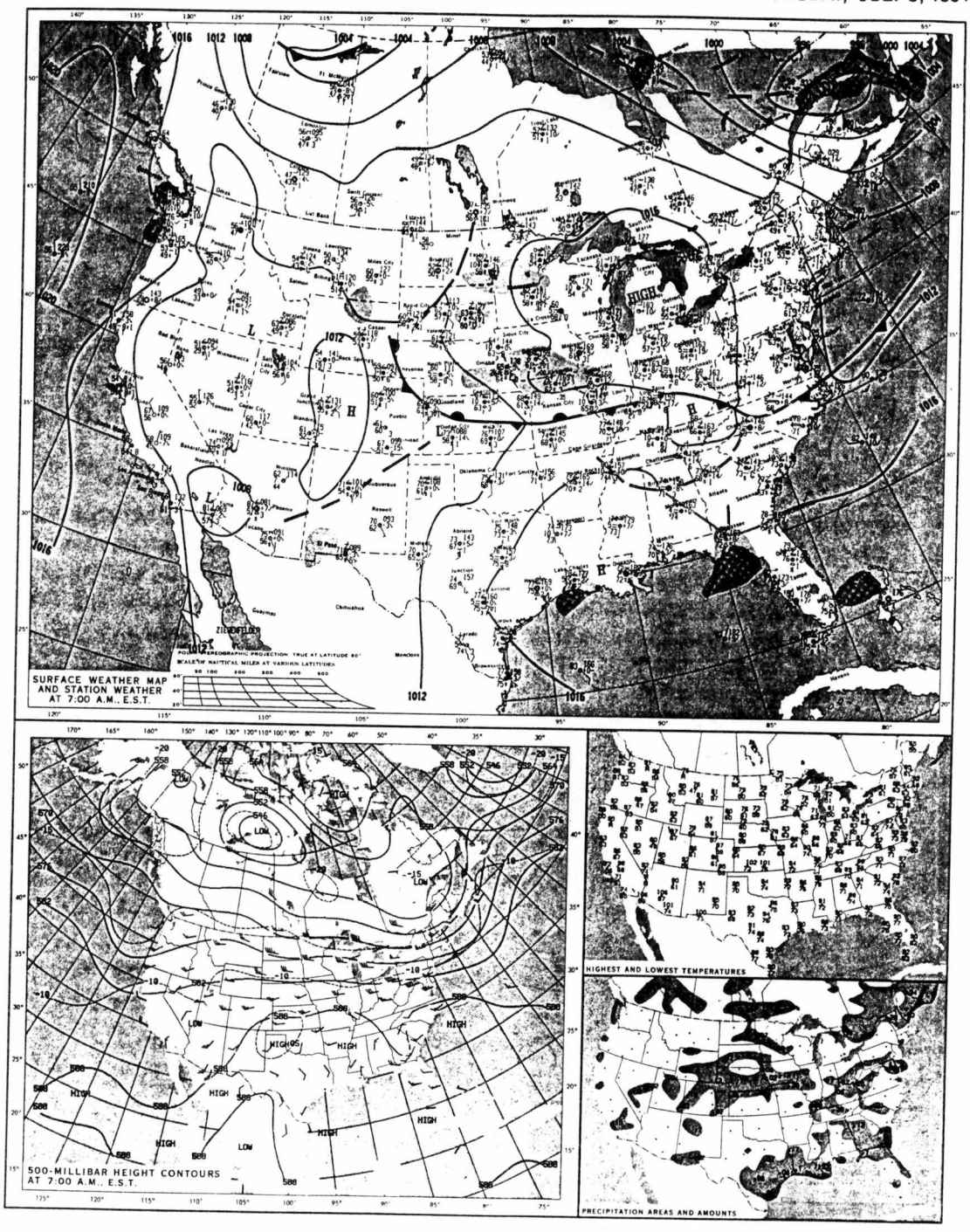


Figure 7-10. Example of the NOAA's "Daily Weather Maps."

Source: Climate Analysis Center. Daily Weather Maps. National Oceanic and Atmospheric Administration. 1992.

7.6 The Effects of the June 11-18 Meteorology on Ozone Concentrations

Meteorological Summary

Figure 7-11 summarizes the locations of high pressure systems with circles and frontal systems with solid and dashed lines for the time period June 10-19, 1988 on four maps. Any two circles on a map with the same hatch pattern indicate anti-cyclones that were present on the same day.

During June 8 and 9, 1988 East Tennessee, Virginia, and Kentucky experienced a lot of frontal activity and rain. On June 10 a new High Pressure air mass began to move into the area with the highest pressures in Wisconsin, Iowa, and Illinois. On June 12, the center of Anti-cyclone had moved to near Bristol Tennessee/Virginia, where it stagnated for several days. The Anti-cyclone weakened considerably on June 16 as a cold front neared Virginia and East Tennessee. On the morning of June 17, the cold front bordered Virginia and East Tennessee, but a portion of the high pressure cell held the front back in Southwestern Virginia, near White Top Mountain and probably also affected Roanoke and Mount Mitchell. By 7:00 am on June 18 the weak front had finally pushed by most all the intensive stations, especially those around the Shenandoah Valley. The two possible exceptions were the Mount Mitchell/Asheville area and Chattanooga (Hamilton County), where it changed to a stationary front. On June 19 the front had dissipated as high pressure returned to the three states.

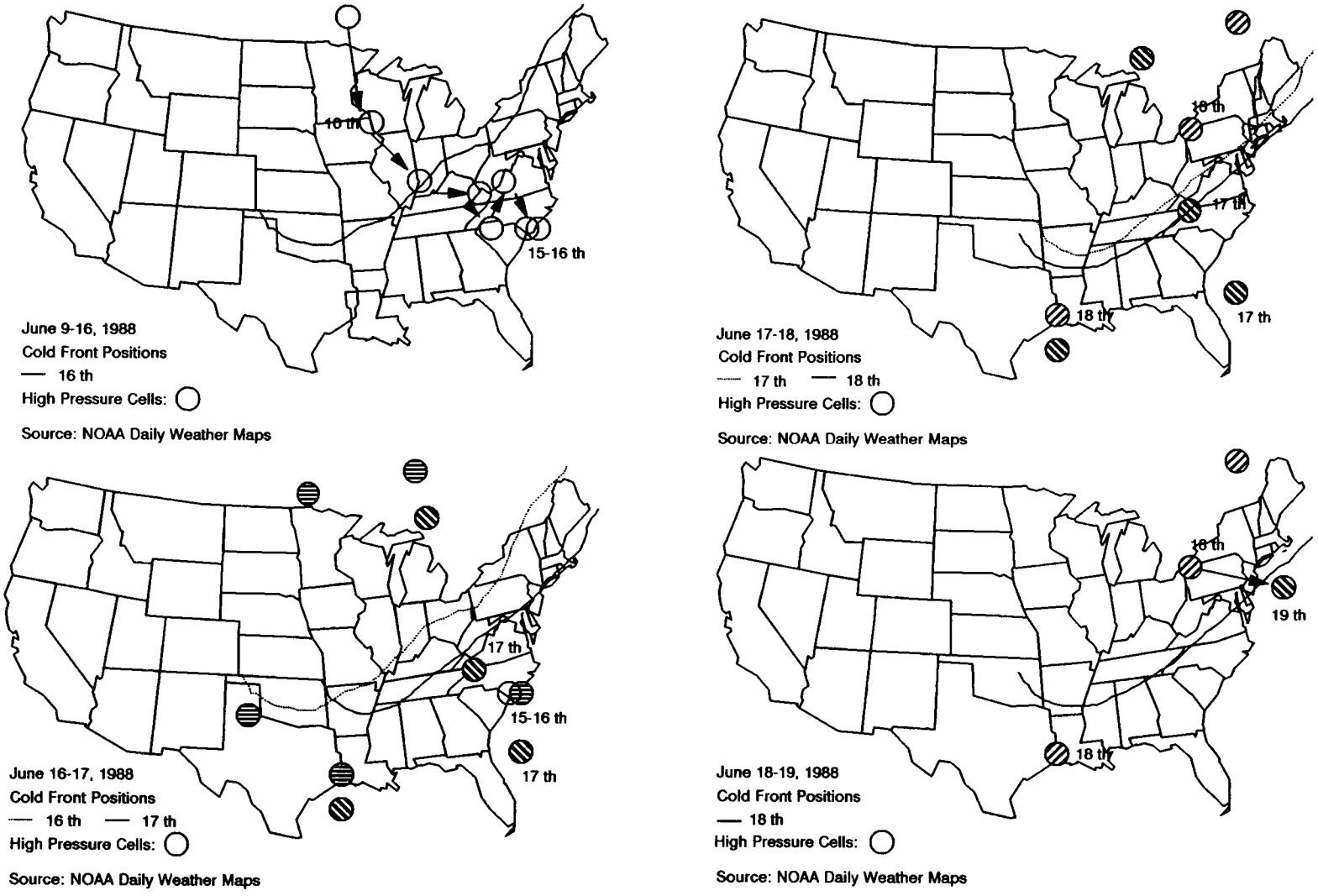


Figure 7-11. Summary of Positions of High Pressure Cells and Frontal Systems for June 9-19, 1988 at 7:00 am.

Intensive Study Ozone Monitors

Four summary graphs of ozone concentrations at representative SBL and RL stations appear in figure 7-12. Graphs of ozone concentrations for specific monitors for June 11-18 are located in Appendix B.

As shown in the graphs in figure 7-12 featuring ozone aloft and in the Shenandoah National Park, observations at RL stations generally were between 40 and 50 ppb very early on June 11. As shown in the other two graphs, SBL stations maximums on that day ranged from 60 to 65 ppb. Concentrations at most stations peaked on June 14 or 15 as the anti-cyclone stagnated. However, beginning on June 16 as the cold front neared various stations, observations were not so homogenous.

As a cold front moved south through the Shenandoah National Park June 17, concentrations in that area also dropped. Being the northernmost monitor, concentrations dropped at Dickey Ridge and then Big Meadows. However, between 4:00 and 6:00 am, June 18, concentrations at Dickey Ridge and Big Meadows began to rise in an apparent example of regional, nocturnal transport as a new air mass moved into the area.

In contrast ozone concentrations at White Top and Mount Mitchell did observe a strong decrease as a portion of the anti-cyclone prevented the cold front moving that far south. Eleven hour dampened concentrations at White Top and daily maximum concentrations at Marion simply made a steady 25 ppb

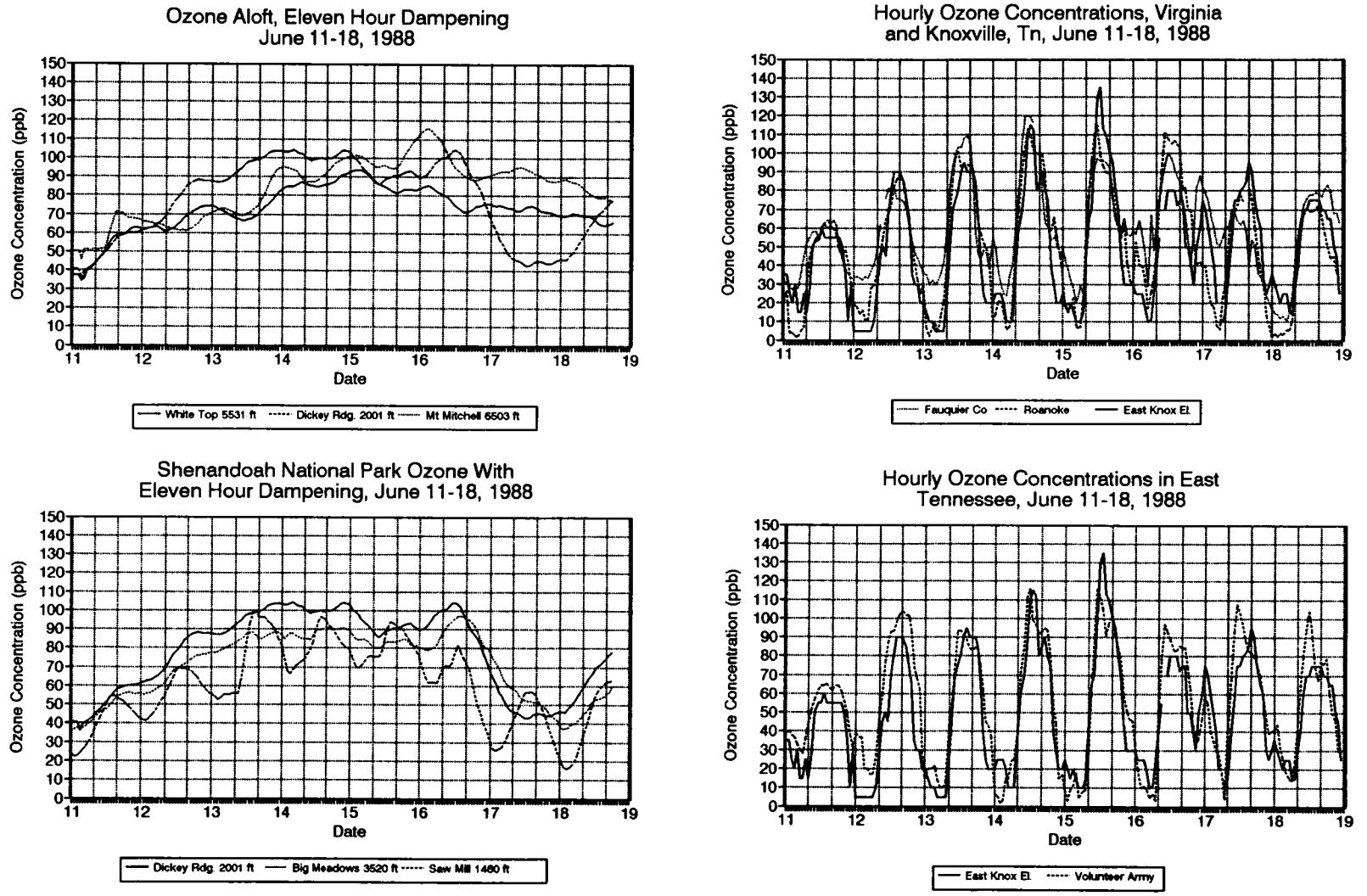


Figure 7-12. Ozone Concentrations at Selected Stations for June 11-18, 1988.

drop from June 15 to June 18 as the high pressure system weakened gradually. Meanwhile, Mount Mitchell reached a peak near 120 ppb near 2:00 am, June 16. Over the next 16 hours concentrations there fell to 90 ppb. The eleven hour average at Mount Mitchell and the daily maximums at Asheville then hovered around 90 ppb for the remainder of the three days as the high pressure stayed more firmly in control of weather there.

Although the SBL masks the effects of the cold front and anti-cyclone at SBL stations, the effects of these meteorological events can still be noted. For instance, as the cold front pushed through the northern parts of Virginia, maximum concentrations at Roanoke and Fauquier County dropped from June 16 to June 17. Meanwhile, in areas of East Tennessee less affected by the cold front, concentrations increased. Further study of the graph of East Tennessee concentrations shows that on June 15 Knoxville and Hamilton County had peak ozone concentrations of 135 and 115 ppb. Over the next three days maximum concentrations in Knoxville were between 75 and 95 ppb, but in Hamilton County, where the front was weaker, maximum concentrations ranged from 96 to 110 ppb.

Ozone Isopleth Maps

The ozone isopleths for June 11-18, 1988, are located in figures 7-13 through 7-20. The contour interval is 10 ppb.

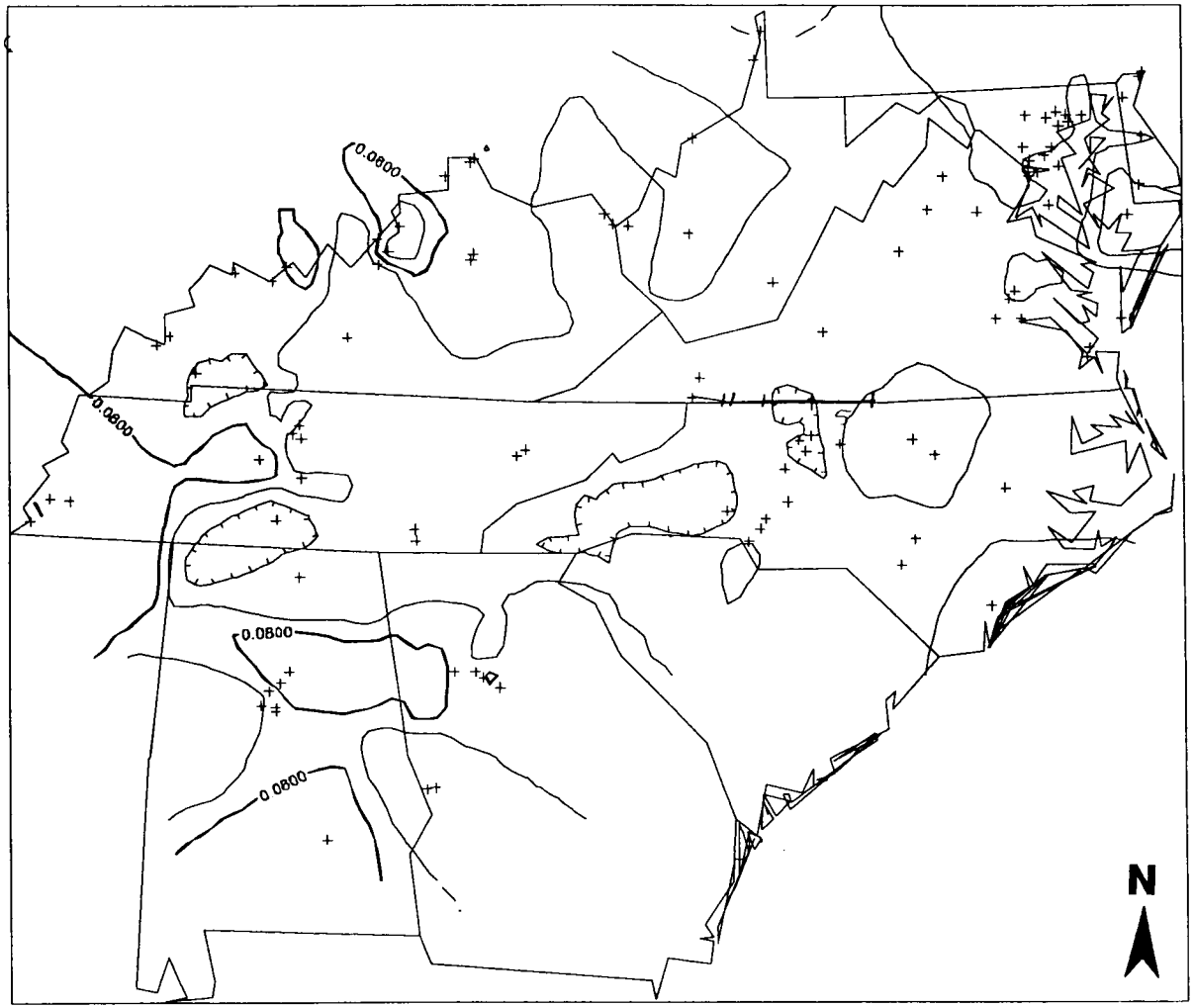


Figure 7-13. Ozone Concentrations in the Southeast June 11, 1988. Contour Interval Is 10 ppb.

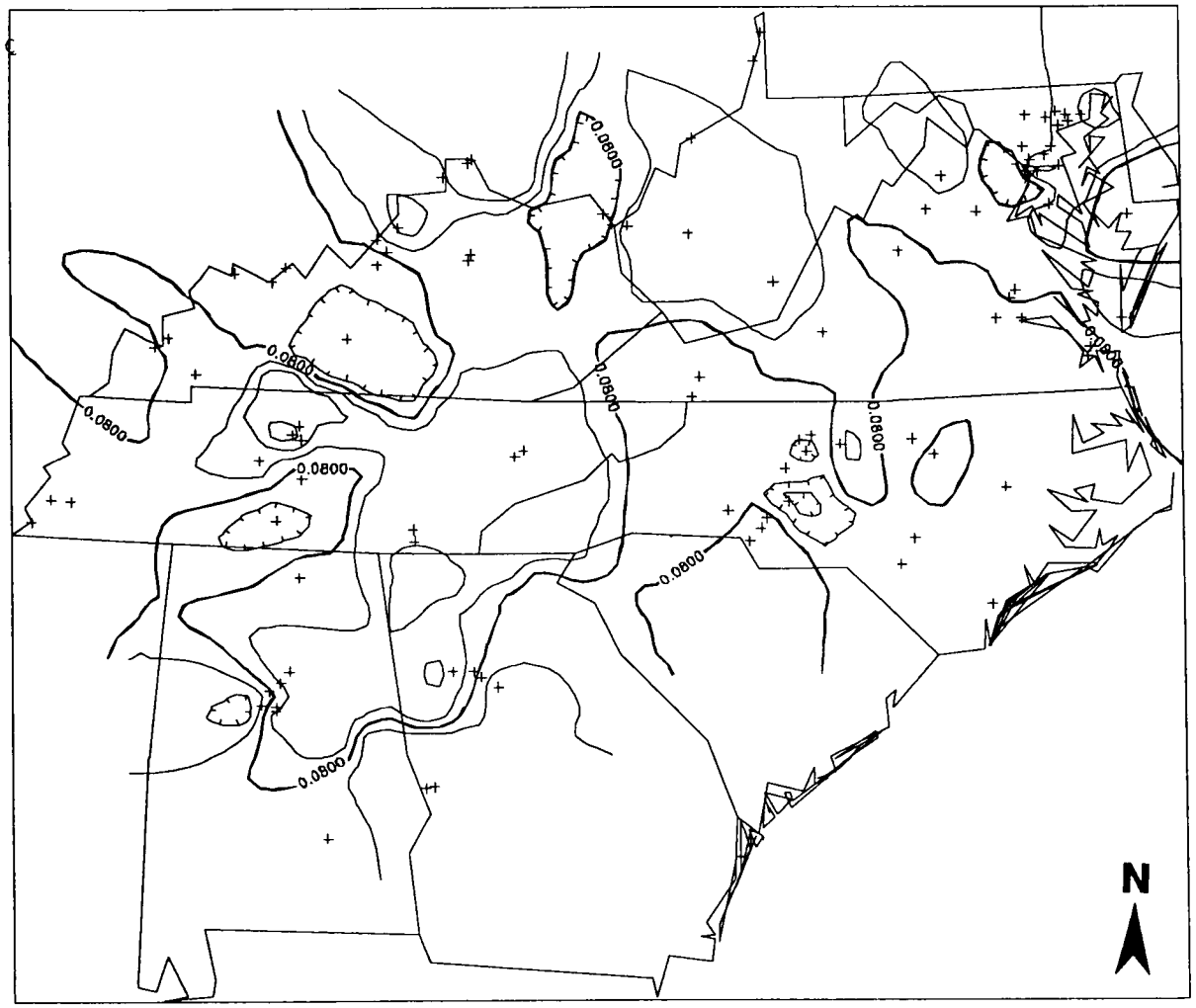


Figure 7-14. Ozone Concentrations in the Southeast June 12, 1988. Contour Interval Is 10 ppb.

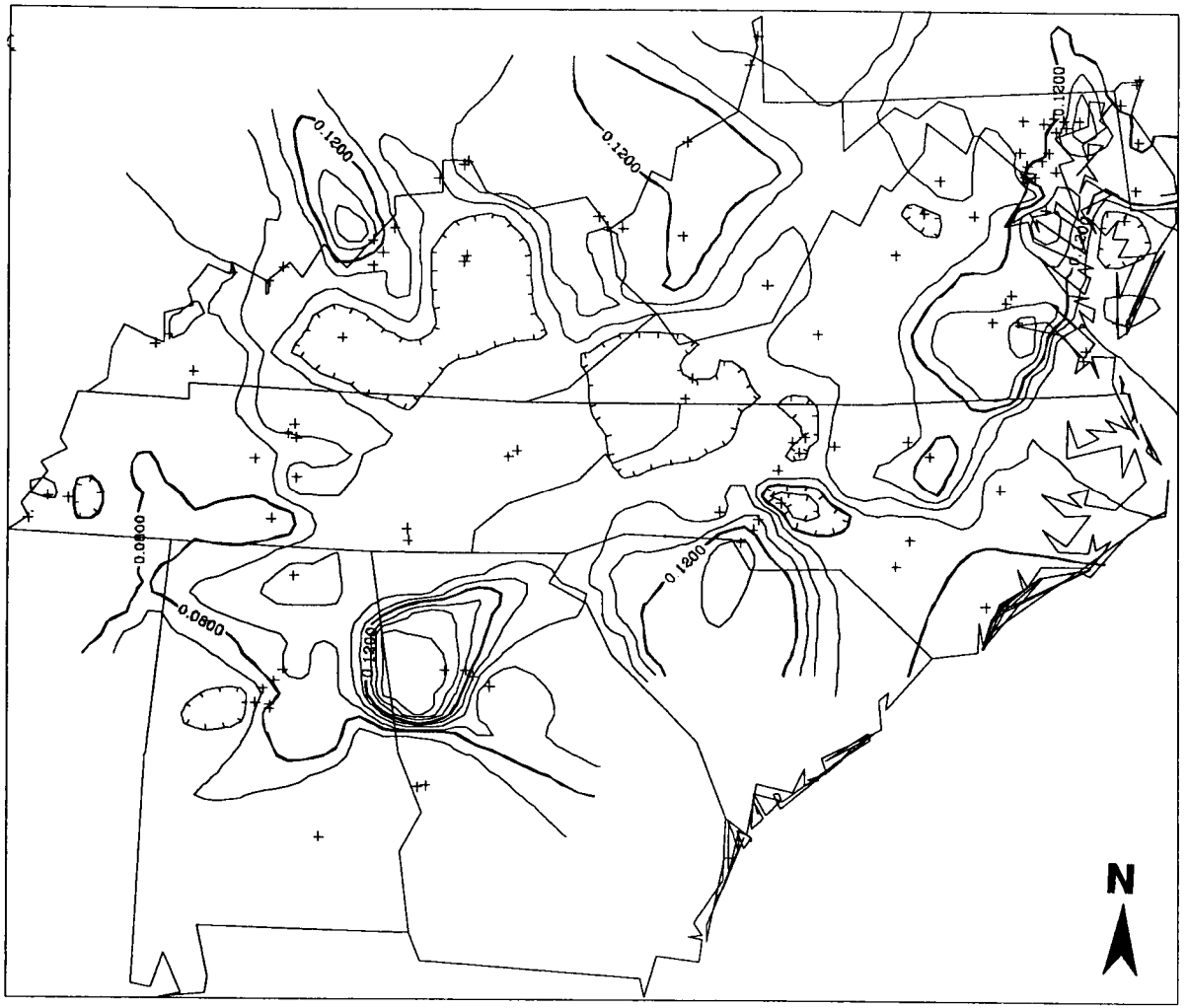


Figure 7-15. Ozone Concentrations in the Southeast June 13, 1988. Contour Interval Is 10 ppb.



Figure 7-16. Ozone Concentrations in the Southeast June 14, 1988. Contour Interval Is 10 ppb.



Figure 7-17. Ozone Concentrations in the Southeast June 15, 1988. Contour Interval Is 10 ppb.

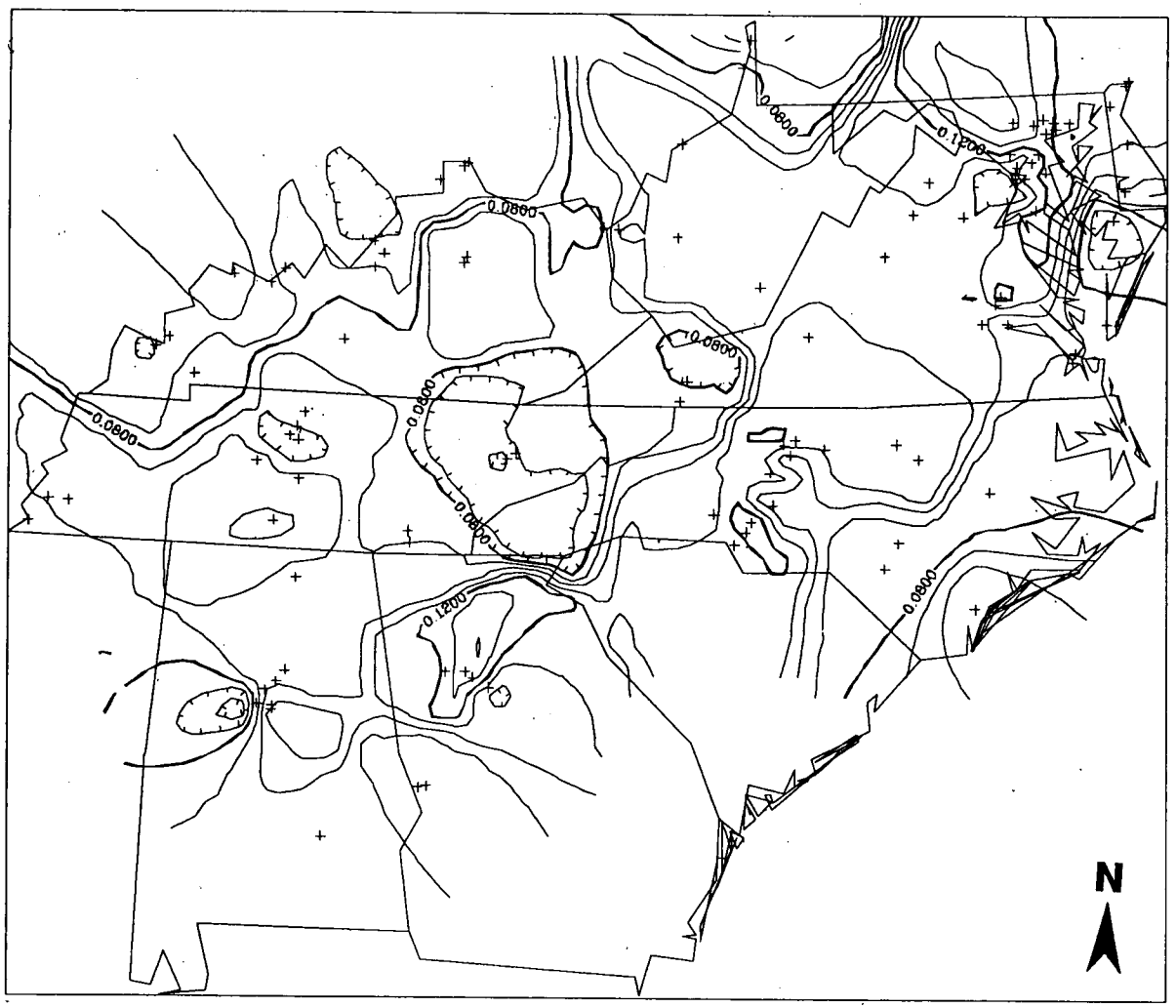


Figure 7-18. Ozone Concentrations in the Southeast June 16, 1988. Contour Interval Is 10 ppb.

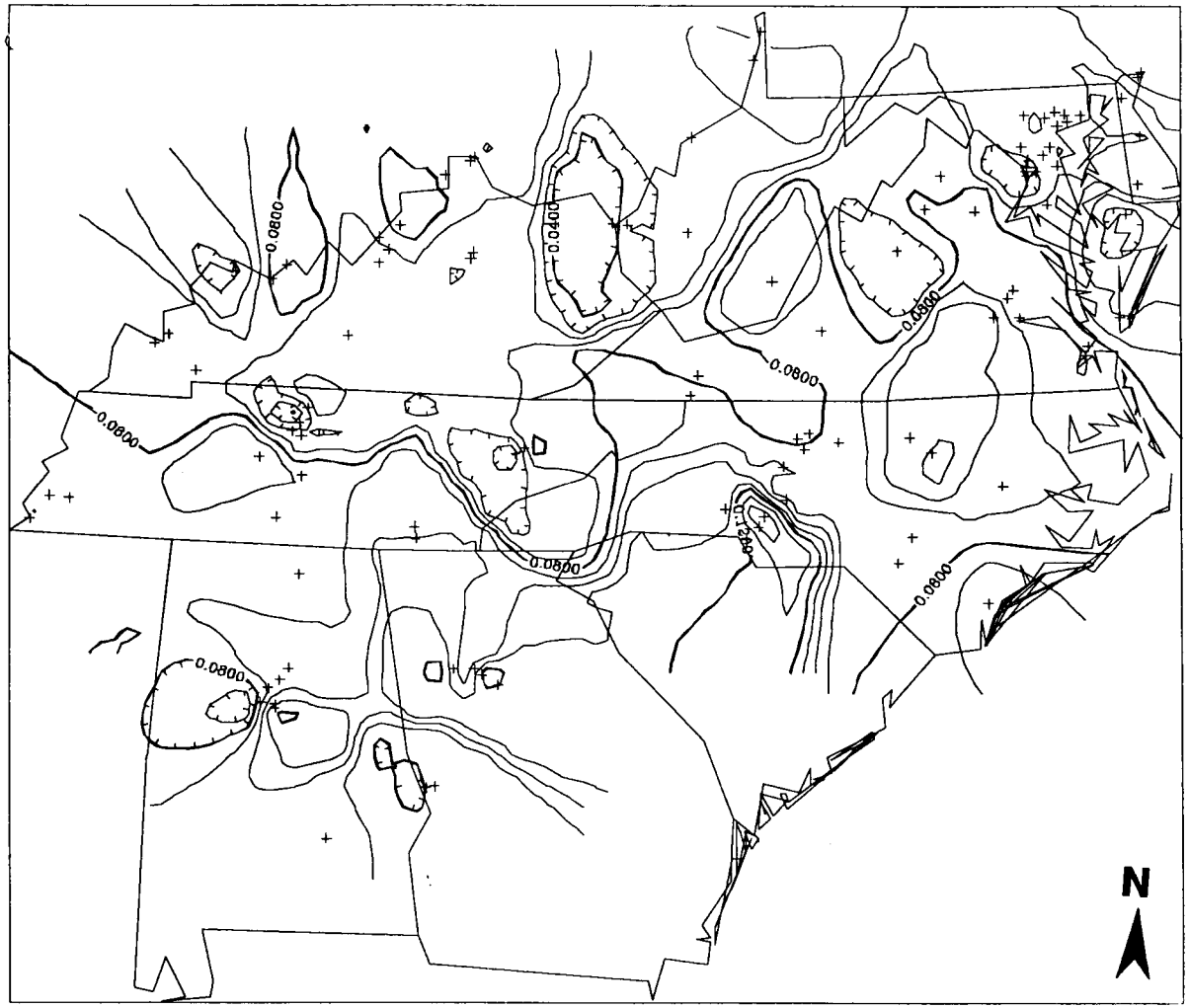


Figure 7-19. Ozone Concentrations in the Southeast June 17, 1988. Contour Interval Is 10 ppb.



Figure 7-20. Ozone Concentrations in the Southeast June 18, 1988. Contour Interval Is 10 ppb.

The center of a new high pressure air mass moved to Southern Illinois and Indiana by June 11, but ozone concentrations in figure 7-13 throughout most of the Southeast were less than 80 ppb. Exceptions include Louisville, Memphis, Birmingham, Montgomery, and a station southwest of Nashville--all of which were less than 100 ppb. No frontal system neared the Southeast until June 16, when a cold front stretched across northwest Kentucky and Tennessee. Meanwhile, as shown in figure 7-15, by June 13 only two small portions, one near Charlotte and another near Birmingham and southern Tennessee were less than 80 ppb. At that time Louisville; Atlanta; Charlotte; Raleigh; Charleston and Parkersburg, West Virginia; and an area from Baltimore to Richmond had over 120 ppb of ozone. On June 14 in figure 7-16, Washington, D. C. and Louisville experienced over 180 ppb. The large area of 120 ppb now extended from near Wilmington to Raleigh. Other areas with similar readings included the North Carolina Triad, Atlanta, Nashville, Parkersburg. Figure 7-17 shows that on June 15, concentrations in North Carolina, Virginia, West Virginia, and Washington dropped, but in Baltimore concentrations rose over 200 ppb. Also an area from Knoxville to Atlanta exceeded 120 ppb.

As the cold front neared the northwest area of the map on June 16, figure 7-18 shows that concentrations dropped below 80 ppb along much of the Ohio River in Kentucky and in much of East Tennessee and Southwest Virginia. Meanwhile Washington

and much of Baltimore fell below 120 ppb. Although most of the Southeast experienced a drop in ozone concentrations, levels did increase in southern and central Alabama and Georgia and central North Carolina. As the cold front continued to move across the Southeast over the next two days, concentrations continued to decrease in figures 7-19 and 7-20 with few examples greater than 80 ppb behind the cold front.

7.7 The Effects of the June 19-27 Meteorology on Ozone Concentrations

Meteorological Summary

Figure 7-21 summarizes the locations of high pressure systems with circles and frontal systems with solid and dashed lines for the time period June 21-27, 1988 on four maps. Any two circles on a map with the same hatch pattern indicate anti-cyclones that were present on the same day.

On June 19 a high pressure system began to influence Virginia, North Carolina, and East Tennessee again. East Tennessee continued to be under the influence of the high pressure air mass through June 26. However, a cold front pushed through Virginia, North Carolina, and Northeastern Tennessee on June 24. The front dissipated by 7:00 am June 25 as high pressure regained control of the intensive study area. Nevertheless, the episode ended late on June 26, or possibly very early June 27 when a stronger cold front pushed through

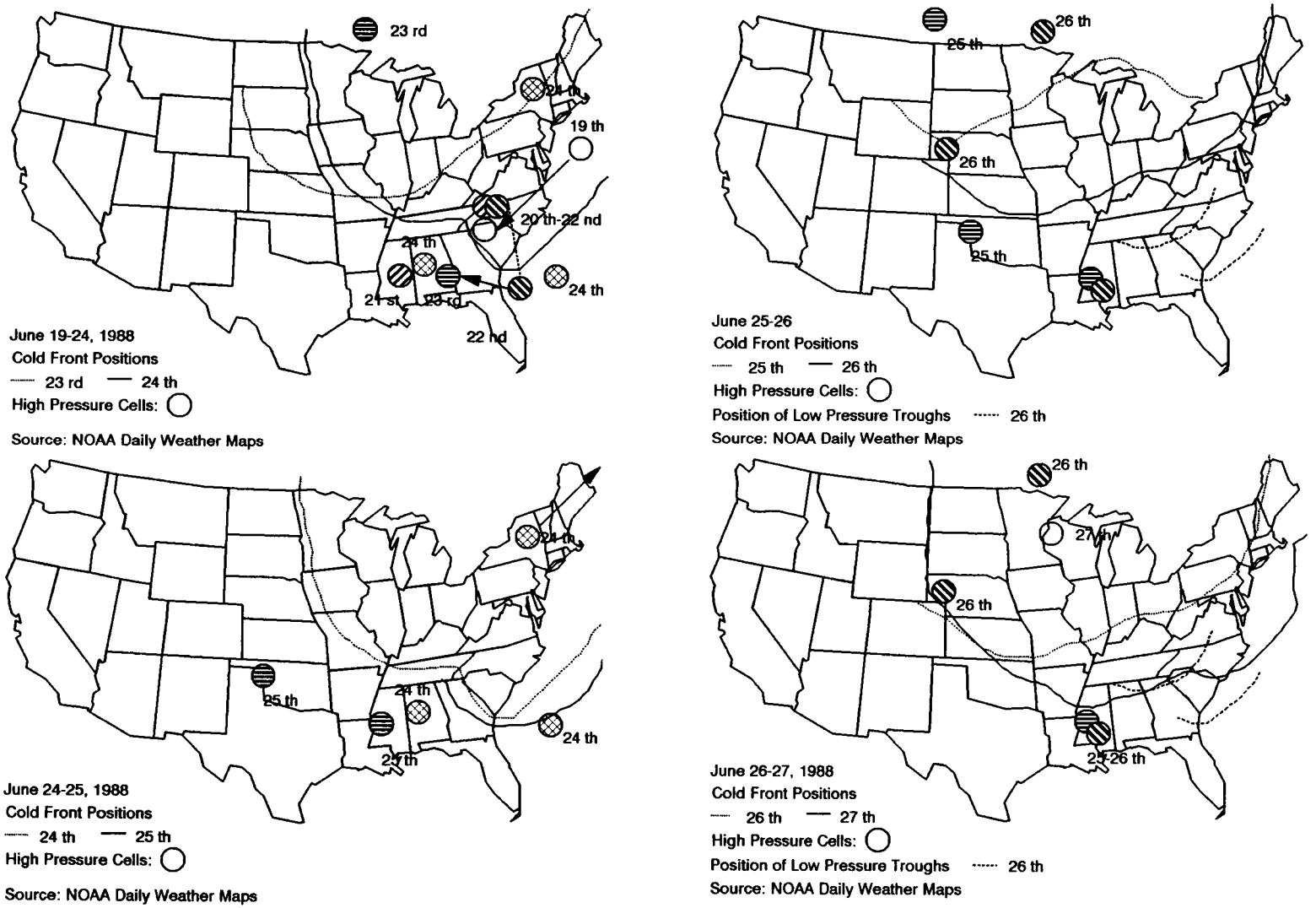


Figure 7-21. Summary of Positions of High Pressure Cells and Frontal Systems for June 19-27, 1988 at 7:00 am.

the entire intensive study area and brought an entirely new air mass to the region.

Intensive Study Ozone Monitors

Six summary graphs of ozone concentrations at representative SBL and RL stations appear in figure 7-22 Graphs of ozone concentrations for specific monitors for June 21-27 are located in the middle column of Appendix B.

As was typical for other stations in the intensive study area, daily maximum concentrations from June 17 to June 21 around Knoxville fluctuated between 75 and 95 ppb. Thus, although concentrations were not exceptionally high they did not show the strong decrease associated with the influx of a new unpolluted air mass. However, as the air mass aged from June 21 through June 23 1988, concentrations increased throughout much of Virginia, North Carolina, and Tennessee as shown in figure 7-22.

Cold fronts began to affect Virginia on June 23 as concentrations in the Shenandoah National Park showed a marked decline in figure 7-22. There was also a marked decline in ozone concentrations in Roanoke as there was no strong mid-day peak in ozone concentrations on June 24 as shown in figure 7-22. In fact, due to the length of time (32 hours) over which concentrations dropped, the front may have stalled and dissipated near Roanoke. However, the only effect of the cold front on data from Fauquier County was to drop the maximum

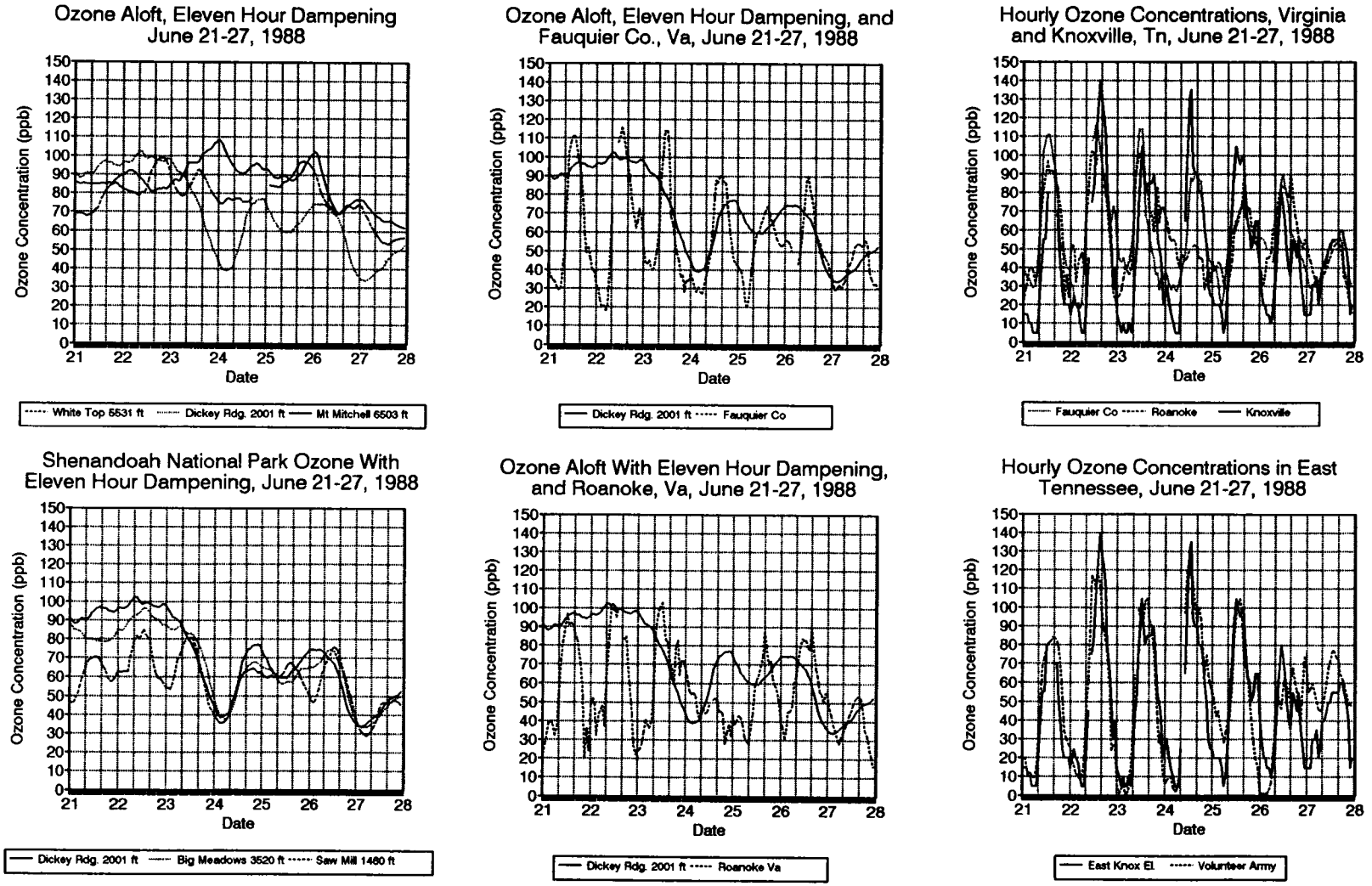


Figure 7-22. Ozone Concentrations at Selected Stations for June 21-27, 1988.

from 115 ppb, June 23, to 90 ppb, June 24. One possible explanation of these events is that since the front moved north to south, it passed through Fauquier County the night of June 23/24 and passed through Roanoke during the day of June 24. However, the cold front did not quite reach White Top and Mount Mitchell. Consequently, the Ozone Aloft graph in figure 7-22 shows that these two stations do not observe the decrease in concentrations that occurred at Dickey Ridge. Finally ending the episode, another set of cold fronts and troughs passed the Shenandoah National Park, White Top, Mount Mitchell, Knoxville and Chattanooga, causing a strong drop in concentrations at all stations, especially Dickey Ridge and Big Meadows. Again the north to south movement of the cold fronts in this episode is apparent in the timing of the drops in concentrations at RL stations, as Dickey Ridge was followed by Big Meadows, then Saw Mill Run, White Top, and Mount Mitchell.

Ozone Isopleth Maps

The ozone isopleths for June 23-27, 1988, are located in figures 7-23 through 7-27. The contour interval is 10 ppb.

After June 18, 1988, no more frontal systems affect meteorology in the Southeast until June 24, 1988. The next ozone isopleth map plotted was June 23, 1988 in figure 7-23. At this time concentrations were above 80 ppb around the Southeast except for southern Maryland, southwestern Alabama,

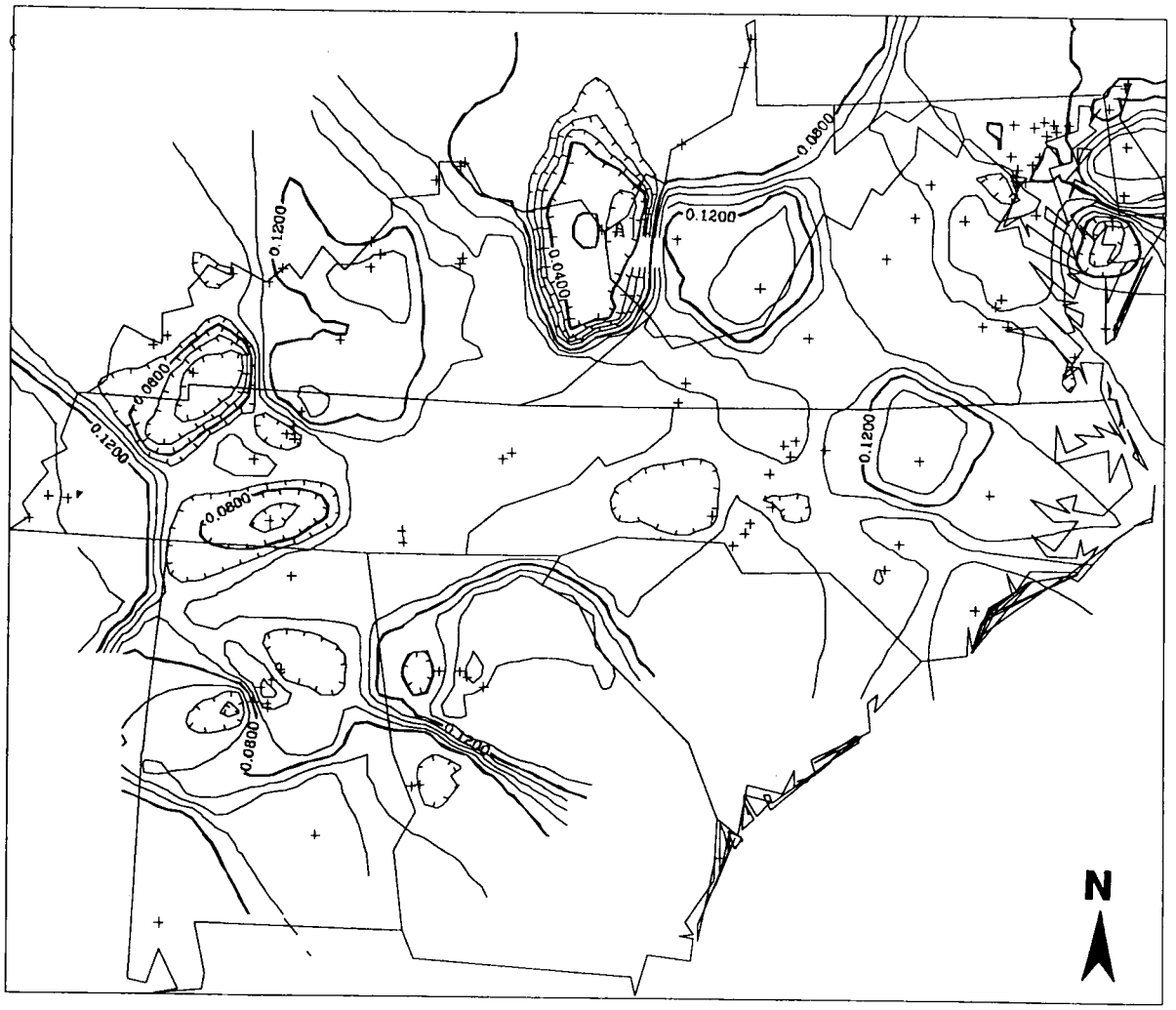


Figure 7-23. Ozone Concentrations in the Southeast June 23, 1988. Contour Interval Is 10 ppb.

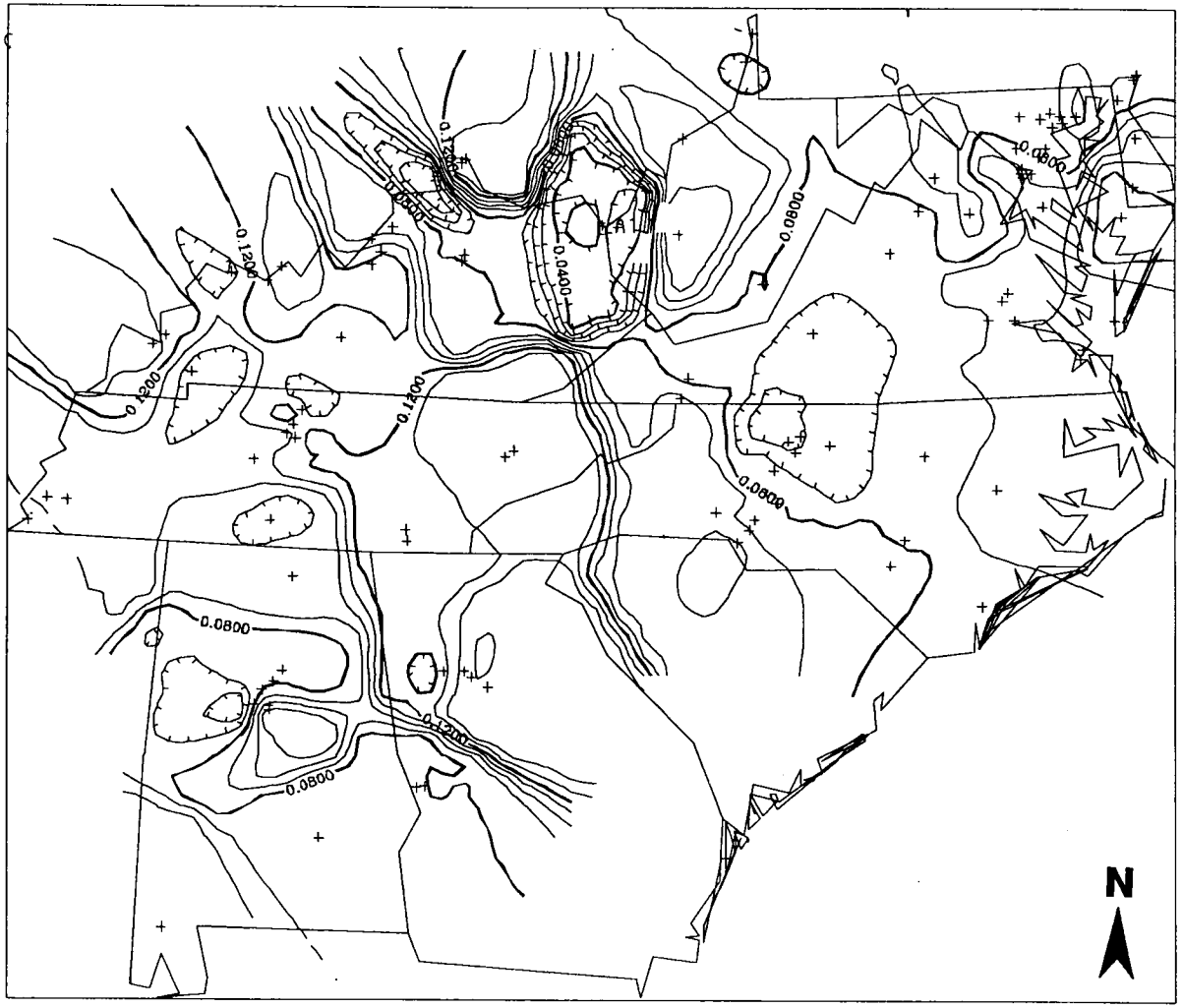


Figure 7-24. Ozone Concentrations in the Southeast, June 24, 1988. Contour Interval Is 10 ppb.



Figure 7-25. Ozone Concentrations in the Southeast June 25, 1988. Contour Interval Is 10 ppb.



Figure 7-26. Ozone Concentrations in the Southeast June 26, 1988. Contour Interval Is 10 ppb.



Figure 7-27. Ozone Concentrations in the Southeast June 27, 1988. Contour Interval Is 10 ppb.

Cincinnati, Ashland, northern West Virginia, and parts of rural Western Kentucky and Middle and West Tennessee. The following day (June 24 depicted in figure 7-24) the front had moved south to South Carolina, central East Tennessee, and the northern edge of West Tennessee. It also lowered ozone concentrations behind it throughout most of North Carolina, the Virginias, Maryland, Delaware, and northeastern Kentucky to below 80 ppb. Areas that had increased ozone concentrations above 120 ppb included an area from Knoxville through Chattanooga to Atlanta. Also concentrations in many areas along the Ohio River in Kentucky showed an increase.

However, in figure 7-25 on June 25 a complicated interaction between ozone and meteorology began. A cold front did not appear until 7:00 am June 26 near the Ohio River border of Kentucky, but ozone concentrations there dropped on June 25 in figure 7-25. As high pressure systems stayed in place in central Alabama, ozone concentrations increased around Atlanta but decreased around Birmingham from June 24-25. Several low pressure troughs passed through the Southeast, and so ozone concentrations stayed below 80 or 90 ppb throughout much of the South on June 26 in figure 7-26. Another cold front passed through to central Alabama and Georgia on June 27; apparently sweeping an area of 130 ppb ozone from near Mammoth Cave, Kentucky in figure 7-26 (June 26), to Montgomery, Alabama the following day in figure 7-27. With the exception of Wheeling, West Virginia, all areas north

of and including Tennessee and North Carolina observed less than 80 ppb of ozone on June 27 in figure 7-27.

7.8 The Effects of the July 1-11 Meteorology on Ozone Concentrations

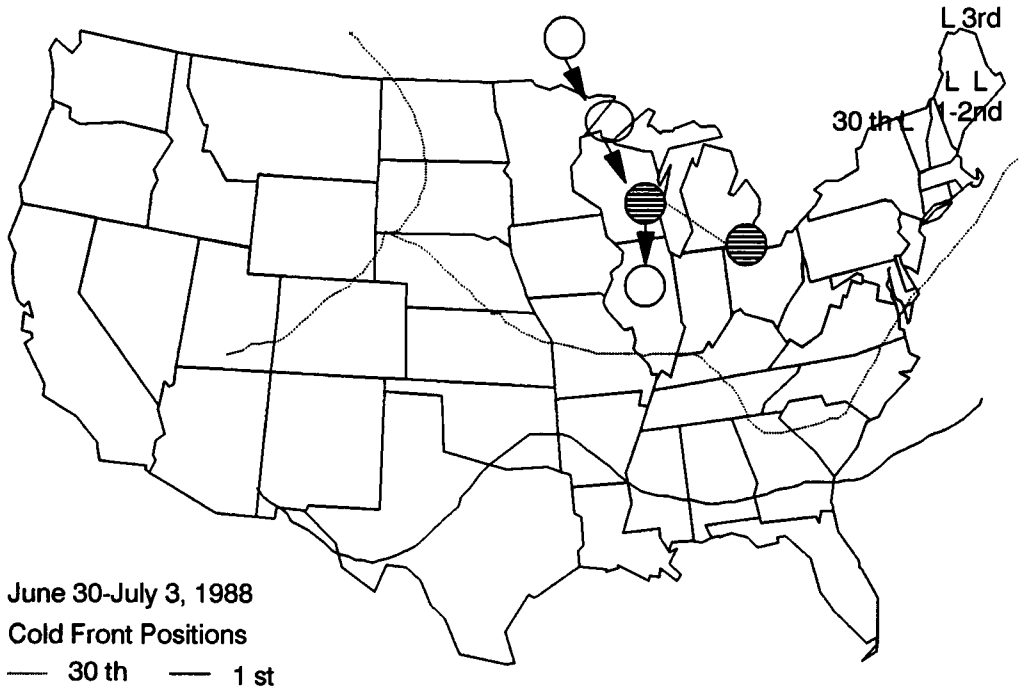
Meteorological Summary

Figure 7-28 summarizes the locations of high pressure systems with circles and frontal systems with solid and dashed lines for the time period June 21-27, 1988 on two maps. Any two circles on a map with the same hatch pattern indicate anti-cyclones that were present on the same day. Low pressure cells are marked by an "L."

The intensive study area experienced another frontal system June 29 and 30 before a weak high pressure air mass began to influence the weather on July 1. However, two low pressure cells dominated weather from Maine to Newfoundland from July 1-3. Even so, a strong anti-cyclone developed off of Nova Scotia on July 4 with no frontal boundary. By July 6 it moved southwest to West Virginia, again with no frontal boundary, where it stagnated in the Southern Appalachians and the Midwest through July 11. By this time the air mass was no longer well defined, but no new air mass moved in to replace it.

Intensive Study Ozone Monitors

Four summary graphs of ozone concentrations at representative SBL and RL stations appear in figure 7-29.



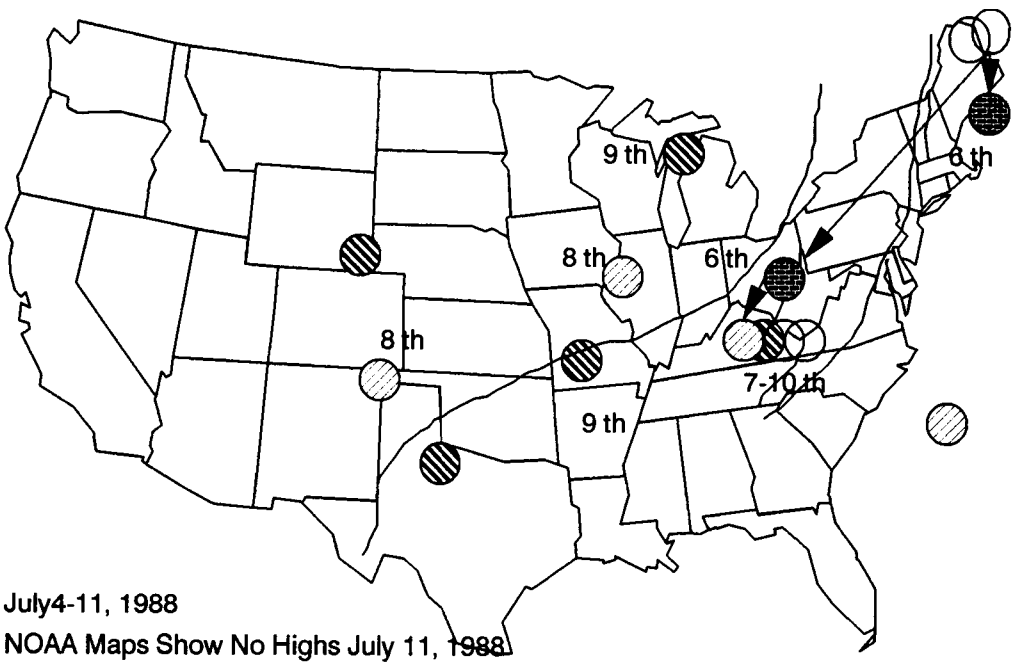


Figure 7-28. Summary of Positions of High Pressure Cells and Frontal Systems for June 30 - July 11, 1988 at 7:00 am.

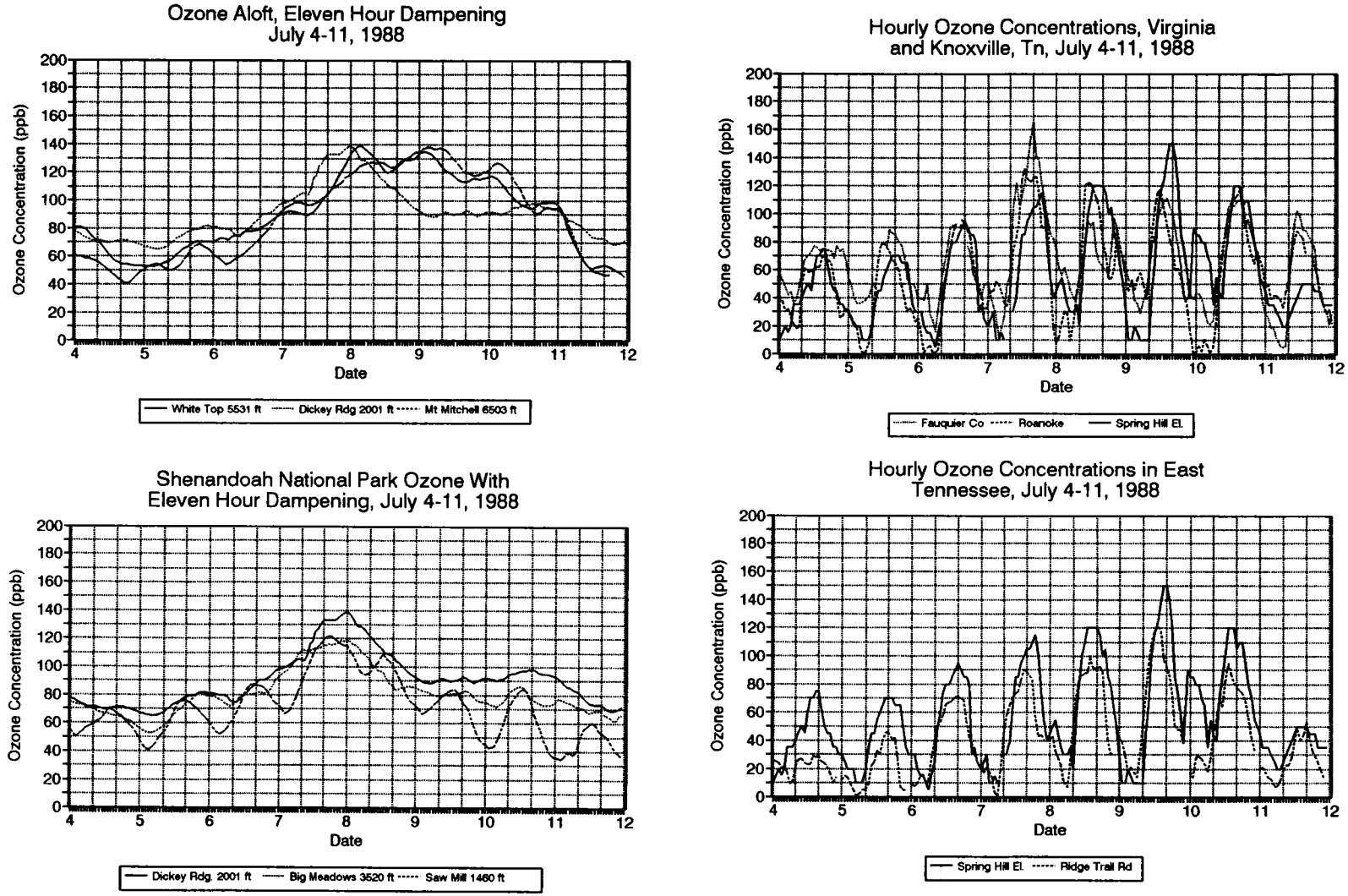


Figure 7-29. Ozone Concentrations at Selected Stations for July 4-11, 1988.

Graphs of ozone concentrations for specific monitors for July 4-11 are located in Appendix B.

Ozone concentrations in East Tennessee were below 80 ppb on June 27, June 30, July 1, and July 3-5. However, as shown in figure 7-29, they began a sharp increase on July 6 that coincides with the movement of the high pressure system from Nova Scotia to West Virginia. Concentrations throughout the intensive study area observed a similar rise in concentrations. Concentrations throughout the Southeast tended to peak on July 8 or 9. Likewise concentrations began to fall sharply over the entire area as the high pressure air mass lost its strength and organization. Thus, most ozone graphs encompassing July 4-11 from the intensive study stations, especially the RL stations, have a roof top appearance with the gable on July 8 or 9.

Ozone Isopleth Maps

The ozone isopleths for July 4-11, 1988, are located in figures 7-30 through 7-37. The contour interval is 10 ppb.

After a new high pressure air mass moved into the Southeast on July 1, 1988, no frontal systems affected southern Meteorology until after June 11. The next ozone contour plotted was July 4, 1988 in figure 7-30. For places exceeding 80 ppb, it shows an area around Memphis and another "V" shaped region extending from central Kentucky, northeast to Pennsylvania, southwest to Washington and Baltimore, and



Figure 7-30. Ozone Concentrations in the Southeast July 4, 1988. Contour Interval Is 10 ppb.



Figure 7-31. Ozone Concentrations in the Southeast July 5, 1988. Contour Interval Is 10 ppb.



Figure 7-32. Ozone Concentrations in the Southeast July 6, 1988. Contour Interval Is 10 ppb.

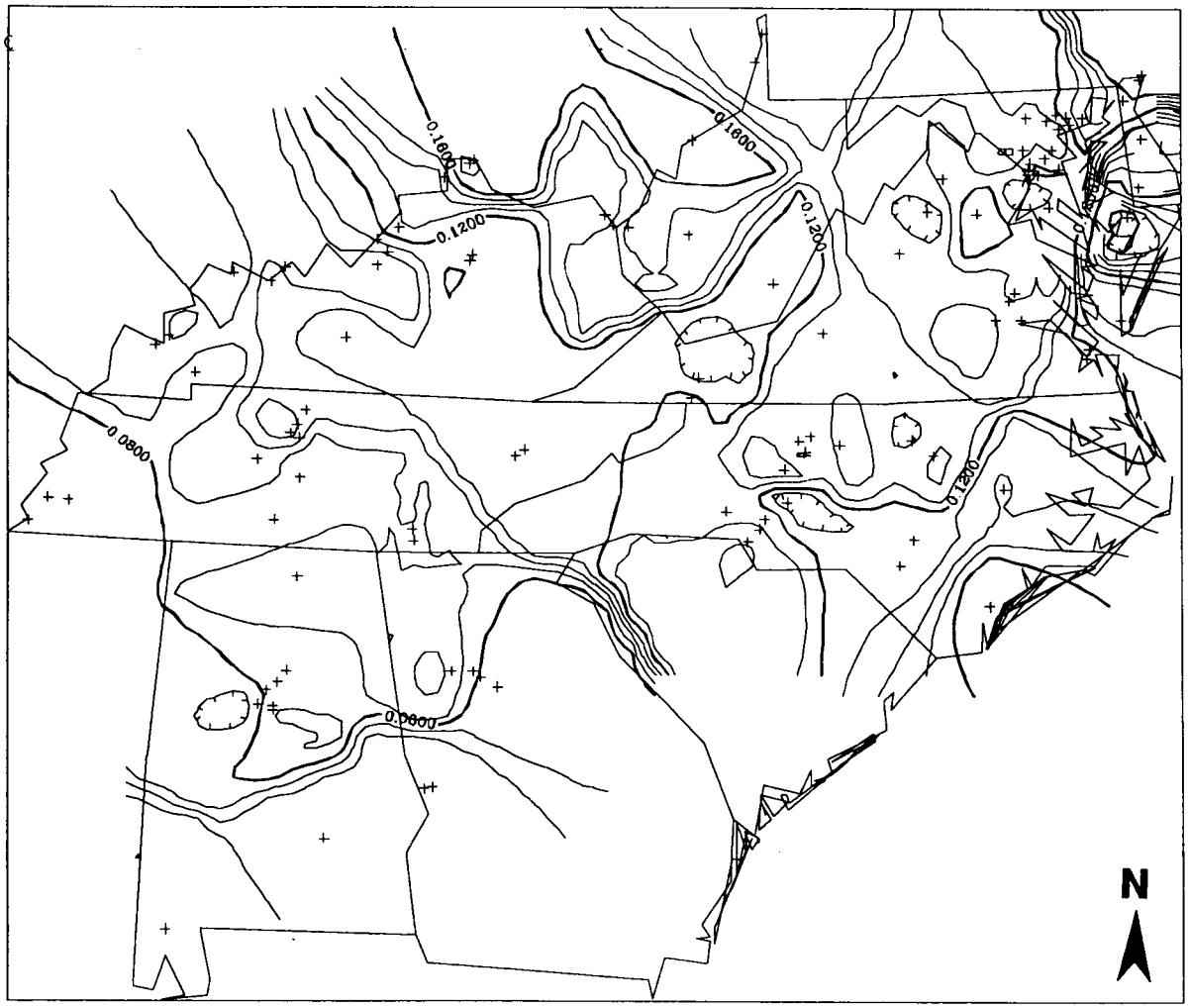


Figure 7-33. Ozone Concentrations in the Southeast, July 7, 1988. Contour Interval Is 10 ppb.

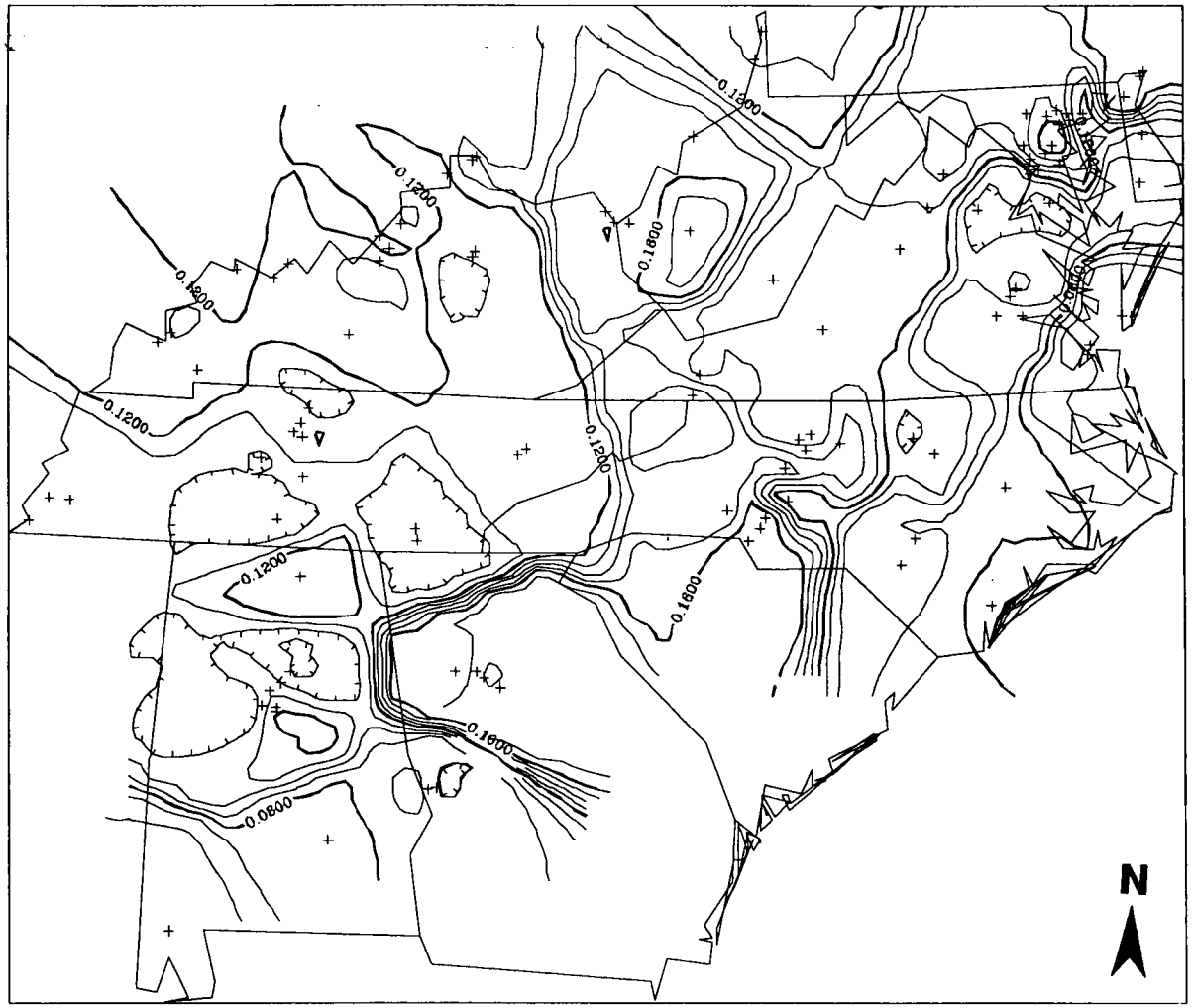


Figure 7-34. Ozone Concentrations in the Southeast July 8, 1988. Contour Interval Is 10 ppb.



Figure 7-35. Ozone Concentrations in the Southeast July 9, 1988. Contour Interval Is 10 ppb.



Figure 7-36. Ozone Concentrations in the Southeast July 10, 1988. Contour Interval Is 10 ppb.

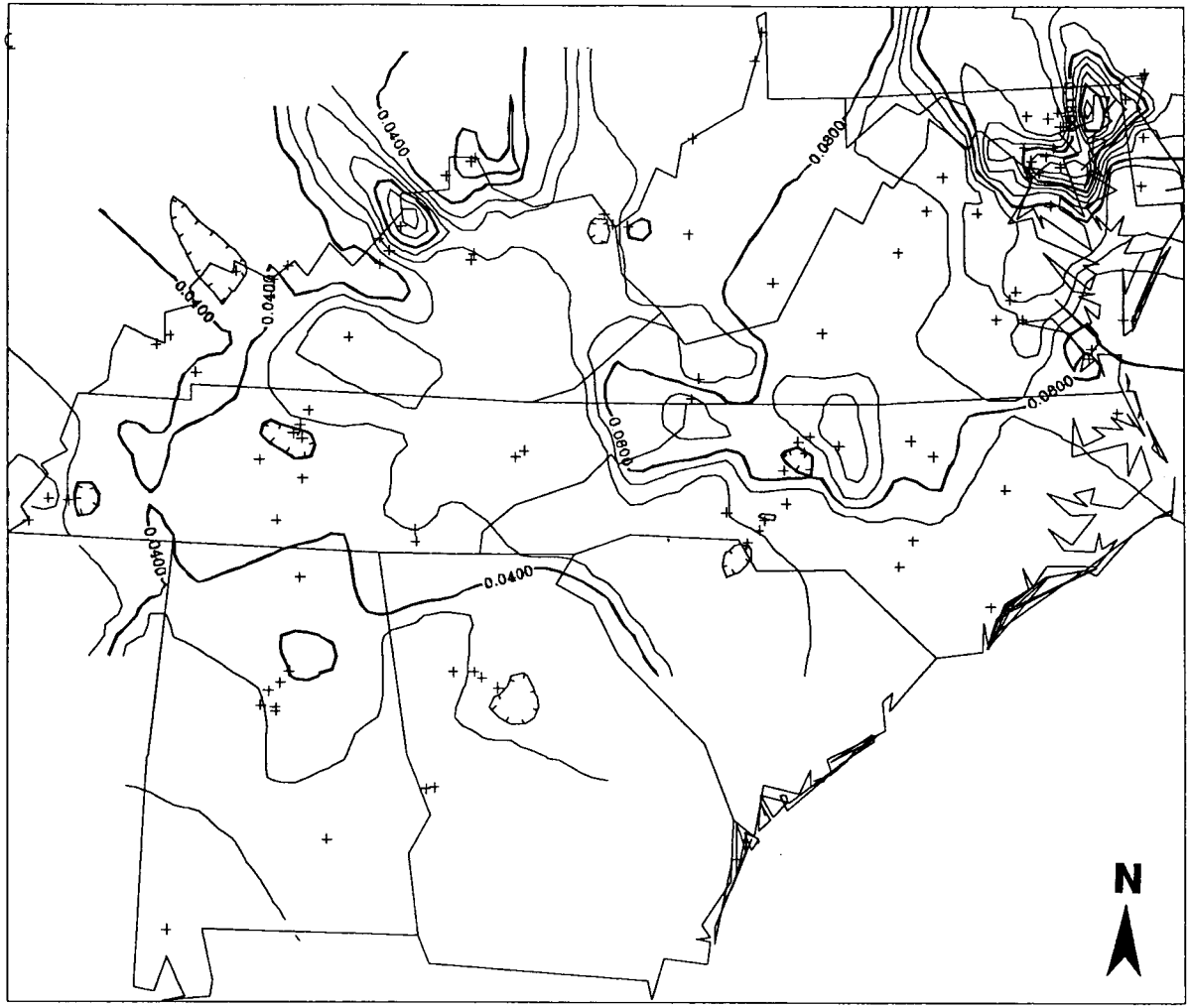


Figure 7-37. Ozone Concentrations in the Southeast July 11, 1988. Contour Interval Is 10 ppb.

then south to through Richmond to North Carolina. The latter region surrounds the Shenandoah Valley, Southwest Virginia, and much of the eastern border of West Virginia. On July 5 in figure 7-31 as the high pressure system moved from Maine to West Virginia, the 80 ppb isopleth moved to incorporate the Shenandoah Valley and a region exceeding 120 ppb developed northwest of Washington and Baltimore. On July 6 in figure 7-32 as the air mass stagnated, the 80 ppb isopleth again moved southwest to include the rest of Kentucky, central East Tennessee, and southwestern North Carolina. Areas exceeding 120 ppb included Parkersburg, Richmond, Washington, and Baltimore, which nearly reached 190 ppb. The following day, the area exceeding 80 ppb grew to include Middle Tennessee, northwest Georgia, and the northern half of Alabama. Furthermore, a "U" shaped area exceeding 120 ppb lay to the north of Marion Virginia, extending from northeastern Kentucky, to the north end of the Shenandoah valley, and down through most of central North Carolina. By July 8 in figure 7-34, the entire map except southern Alabama and the eastern edges of Virginia and North Carolina exceeded 80 ppb. Also the area exceeding 120 ppb grew to include most of Kentucky, and northeastern Tennessee. Areas clearly exceeding 160 ppb included Atlanta, Charlotte, Baltimore, and Charleston West Virginia. On July 9 in figure 7-35, as the anti-cyclone continued to move west, the 120 ppb isopleth slid by Knoxville and Chattanooga and surrounded an area including central and

Eastern Kentucky (except Lexington), most of West Virginia, Marion and White Top, Atlanta, and central and Western North Carolina (except part of Charlotte). Thus, central and western Virginia, Atlanta, and Charlotte all observed a decrease in ozone concentrations. Washington and Baltimore continued to exceed 160 ppb.

As the high pressure finally began to weaken on June 10, areas in the western portion of the graph began to observe rain and less than 80 ppb and areas in figure 7-36 exceeding 120 ppb were limited to East Tennessee, major metropolitan areas in North Carolina, and an area from Richmond to Wilmington. Then as more rain fell on the south on July 11, the only area observing more than 80 ppb were just around and to the northeast of Virginia in figure 7-37.

7.9 Conclusions

The relatively constant ozone concentrations observed at RL stations indicates that NO_x scavenging and ground deposition do not have a strong impact on concentrations at these stations and in the RL. Also the RL acts to store and transport ozone over large areas. This fact is collaborated by the extensive areas in the isopleth maps that show areas with ozone concentrations greater than 80 or even 120 ppb. Since the RL evolves from the ML, these peak concentrations observed at the ground would be present in the RL as well.

Furthermore, when stations as far apart as Dickey Ridge and Mount Mitchell experienced the same high pressure cells and cold fronts, the graphs of their ozone concentrations had the same shape.

For an example of the potential effects of the storage and transport of the ozone in the RL on ozone concentrations observed at RL and SBL stations consider the 90 ppb eleven hour average from midnight to 8 am at White Top Mountain on July 7, 1988. Assuming a light breeze of 10 mph and eight hours of travel in the RL in a constant direction, then each parcel passing White Top has traveled 80 miles. Then these observations represent an area 80 miles long that had an average daily maximum concentration of 90 ppb on July 6 and another area as much as 80 miles long that will have almost 90 ppb of ozone in the RL above it the morning of July 7. As the ML grows the following morning and entrains these high concentrations, this RL would be an important source of ozone for many communities.

Section 5 on the May Episode and graphs comparing Roanoke and Saw Mill Run show that vertical mixing plays an important role in ozone observations in the RL and the ML. Those results showed that ozone at a low level RL station could decrease in concentration as the ML first began to reach the station. After reaching equilibrium through vertical mixing with concentrations at lower elevations, there is often very little difference in morning and afternoon ozone

concentrations at the lower elevation RL station and a nearby SBL station.

To quantify the potential effects of the entrainment of ozone in the RL by the ML, an 11 hour dampened ozone concentration has been developed for RL stations to include the current hour, the 5 previous hours, and the 5 following hours. While this moving average does not completely remove the strong drop in ozone concentrations due to the SBL or early morning mixing at lower altitude stations like Saw Mill Run, it does remove many of the small peaks and valleys in data at higher altitude stations and create a regional background concentrations. Consequently it makes possible an easy comparison of ozone concentrations at high altitude RL stations and nearby SBL stations. Using this technique it has been found that daily maximum concentrations at SBL stations are often within 5 to 20 ppb of the simultaneous concentrations at Dickey Ridge, White Top Mountain, and Mount Mitchell. These RL stations do not normally experience any strong decreases or increases in concentrations due to vertical mixing and are from 20 to 200 miles away from the SBL station they are being compared to. The consistency of these results over distances of up to two hundred miles, the constant ozone concentrations at RL stations, and the even spread of ozone concentrations in the isopleth maps, demonstrate that large areas of the Southeastern United States experience similar high concentrations in the RL and then in

the ML due to vertical mixing. Thus these three episodes show that Knoxville is most likely to exceed the AQS for ozone when background concentrations in the RL exceed 80 to 120 ppb during the night and early daylight hours over areas of several hundred square miles.

Differences in ozone concentrations observed in graphical comparisons of just 2 or 3 monitoring stations and differences in concentrations in the isopleth maps can often be attributed to specific meteorological events. High ozone concentrations at RL and SBL stations seem to depend on the existence of a high pressure air mass which dominates the air quality at the monitoring stations being compared. A weakening in the high pressure air mass often reduces ozone concentrations. Furthermore, frontal systems and low pressure areas mark boundaries for air masses and can cause a dramatic decrease in ozone concentrations as they pass through an area. The new air mass that follows these systems often increases ozone concentrations considerably compared to observations during the passage of the frontal system. However, the immediate rebound in concentrations after cold fronts tends to be less than the observations before the frontal system passed through the area. When the new air mass moves into an area during the night, a nocturnal increase in ozone concentrations is often observed at RL stations, but not at SBL stations. Often these changes in concentrations due to meteorological systems are only obvious in the RL station data, especially the 11 hour

dampened data. At SBL stations, the nocturnal deposition and scavenging of ozone in the SBL often masks these effects. Thus, the primary process that affects the shape of graphs of ozone concentrations at the higher RL stations are frontal systems and high pressure systems, whereas SBL stations are primarily affected by vertical mixing.

Although it may seem improbable that the RL would have such an impact on the ML, there is far more ozone in the RL than in the ML. The RL can typically be 6000 feet thick while the SBL is only 600-1500 feet thick; also only the SBL is dominated by scavenging or deposition. Thus, the SBL represents only a small portion of a vertical column of air in the boundary layer, and the 5-20 ppb of ozone observed at SBL stations at night is superficially low compared to the potential for over 100 ppb in the much deeper RL. Thus, fundamental meteorology supports the importance of RL ozone on observations at SBL stations.

8.0 CONCLUSIONS

The important conclusions from this thesis are summarized below.

1) Ozone episodes in Knoxville, Tennessee, generally last about 7 or 8 days. The beginning and end of these episodes is usually marked by low ozone concentrations and the passage of a cold front, low pressure system, or a general weakening of the influencing high pressure system.

2) All exceedences of the AQS for ozone have occurred during high pressure systems that stagnated for several days near Tennessee in Kentucky, Virginia, North Carolina, South Carolina, Georgia, Alabama, Mississippi, Louisiana, or off the coast of these states.

3) For the years 1988, 1990, 1991, and 1992, there seems to be little correlation between ozone concentrations and high pressure trajectories. Typical origins of high pressure systems were west of Tennessee, the Midwest, the Northeast, and the Gulf of Mexico.

4) The clear skies associated with anti-cyclones, promote the development of the SBL and RL. Thus, they promote the nocturnal storage and transport of ozone. In contrast the clouds associated with cold fronts and low pressure areas, do not allow these processes to occur.

5) As a high pressure air mass moves into an area, it can increase ozone concentrations over a 12 hour span by over

80 ppb above the concentrations in the preceding cold front or low pressure area.

6) Average background ozone concentrations in a high pressure system can exceed 80 or even 100 ppb.

7) Ozone in the RL can exceed 120 ppb.

8) Ozone concentrations observed at higher altitude RL stations similar to Dickey Ridge and Mount Mitchell experience little NO_x scavenging or ground deposition. Instead their concentrations are dominated by major meteorological events like high pressure cells and cold fronts.

9) Ozone concentrations observed at SBL stations drop to 5-20 ppb during the formation of a SBL due to NO_x scavenging and ground deposition. The following morning vertical mixing increases the observed ozone concentrations dramatically.

10) The altitude of certain RL stations similar to Look Rock and Saw Mill Run are too high to experience the strong ozone depletion associated with SBL stations. However, they can observe a strong decrease in ozone concentrations as the growth of the ML mixes lower ozone concentrations at the ground with higher concentrations at their altitude. After the air surrounding these stations is homogenized with the air below them, the observations will be the same as nearby SBL stations until the SBL forms again.

11) White Top and Mount Mitchell do not appear to experience these same effects (as listed in conclusion 10.) because these monitoring stations lie near the top of the ML

and RL. Thus, by the time the mixed layer grows to their height ozone concentrations are relatively stable.

12) The daily maximum concentrations in rural areas have been observed to be within 5 to 10 ppb of the 11 hour dampened background ozone concentration observed at RL stations within 20 miles.

13) The daily maximum concentrations near medium sized cities such as Knoxville, Roanoke, and Asheville were found to be within 20 ppb of the 11 hour dampened background ozone concentration observed at RL stations within 200 miles.

14) For broad areas of the Southeast, dramatic differences in ozone concentrations observed at separate stations can be attributed to the impacts of different major meteorological episodes like high pressure air masses and cold fronts.

15) The nocturnal ozone depletion and the strong static stability at SBL stations can create a false impression that ozone concentrations throughout the boundary layer are low. Thus, it also masks the effects of major meteorological events such as high pressure systems that may use the RL to transport large concentrations of ozone into the vicinity of the SBL station.

16) When RL stations like Dickey Ridge and White Top experience 11 hour dampened concentrations greater than 80 or 120 ppb, these concentrations are representative of an area of several hundred square miles.

17) Knoxville has exceeded the AQS for ozone when an area of several hundred square miles in the RL experiences ozone concentrations of 80 to 120 ppb.

18) The average difference between daily maximums at Knoxville and the simultaneous 11 hour dampened concentrations at White Top Mountain and Mount Mitchell is less that 20 ppb.

These results and conclusions demonstrate that high pressure systems and the RL combine to concentrate, store, and spread ozone and its precursors over large distances and land areas of several hundred square miles. For any single day the ozone stored in the RL can dominate photochemical production which occurs in the ML. However, the origin of this RL ozone has not been determined even though estimating the background ozone concentration is an important part of any ozone control strategy. Thus, more research is needed to determine if these high RL concentrations are the result of local production in the vicinity of the monitor accumulating over several days, regional transport from larger metropolitan areas, or the accumulation of pollution from the many square miles of surface area that the air mass has traveled before reaching the monitor.

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BIBLIOGRAPHY

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APPENDICES

APPENDIX A

High Pressure Air Mass Trajectories

Legend for Graphs in Appendix A



High Pressure Cells Marked on the NOAA Daily Weather Maps with "H" or "HIGH" (Circles with the Same Hatch Marks Occur on the Same Day)

h — Areas with Barometric Pressure Greater than their Surroundings, but not Marked on the NOAA Daily Weather Maps with "H" or "HIGH"

L — Low Pressure Cells



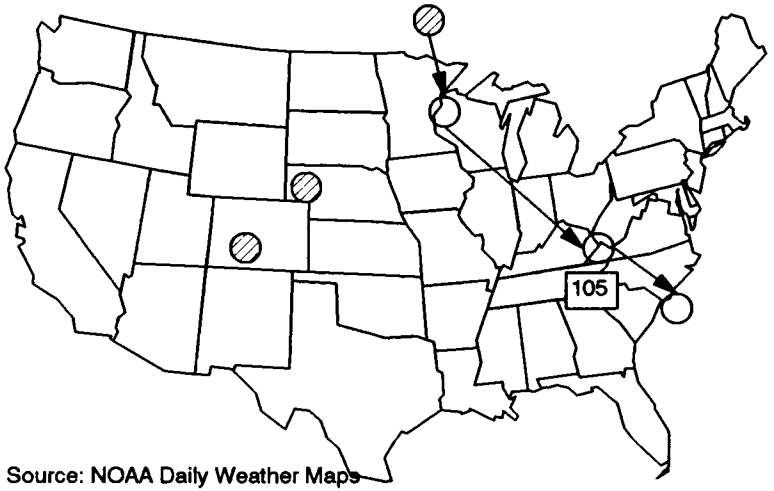
Lines Represent Cold, Warm, or Stationary Fronts



Maximum Ozone Concentrations in ppb in Knox County for the Episode Date

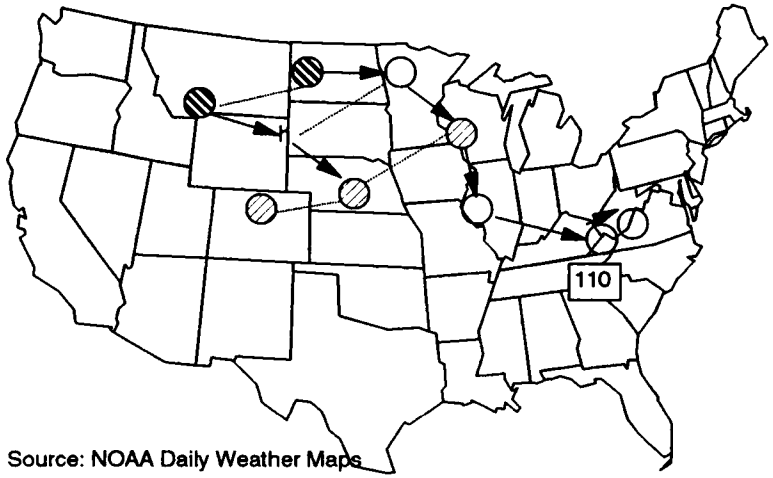
Mid-Westerner Trajectories

High Pressure Air Mass Impacting Air Quality in Knoxville
Four Day Trajectory Ending June 29, 1988



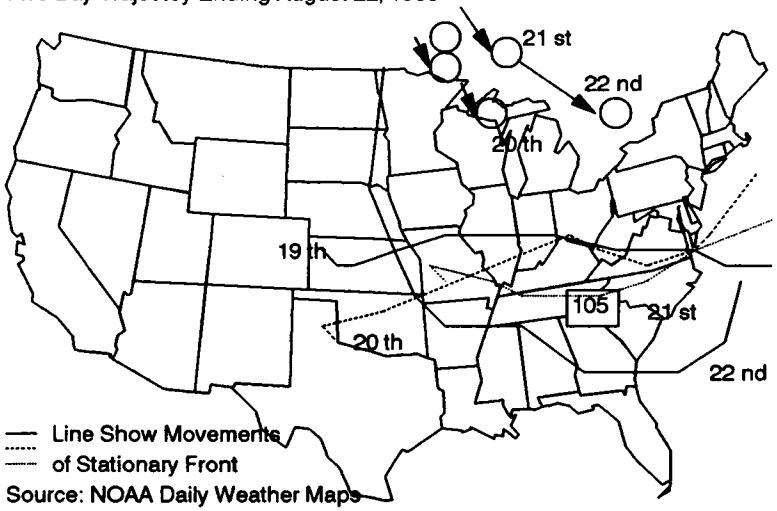
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Six Day Trajectory Ending July 29, 1988



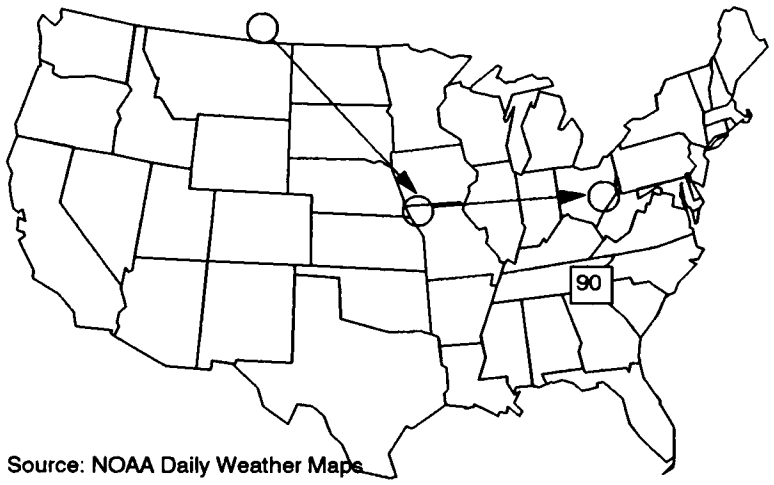
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Five Day Trajectoy Ending August 22, 1988



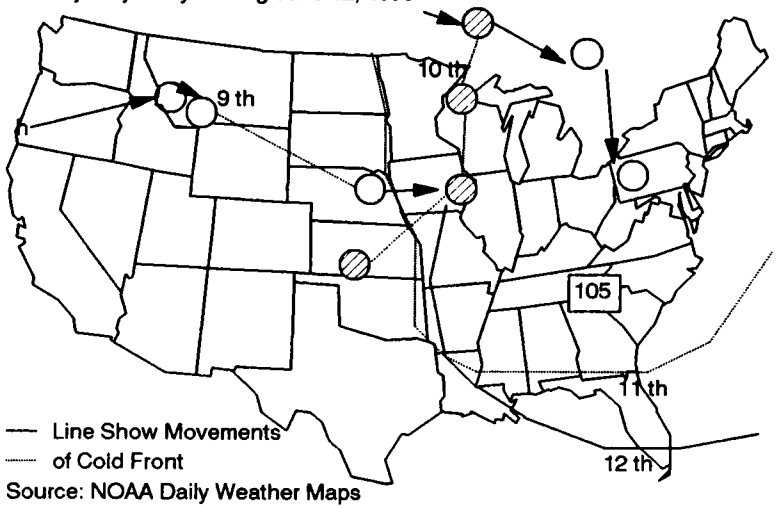
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Three Day Trajectory Ending June 5, 1990



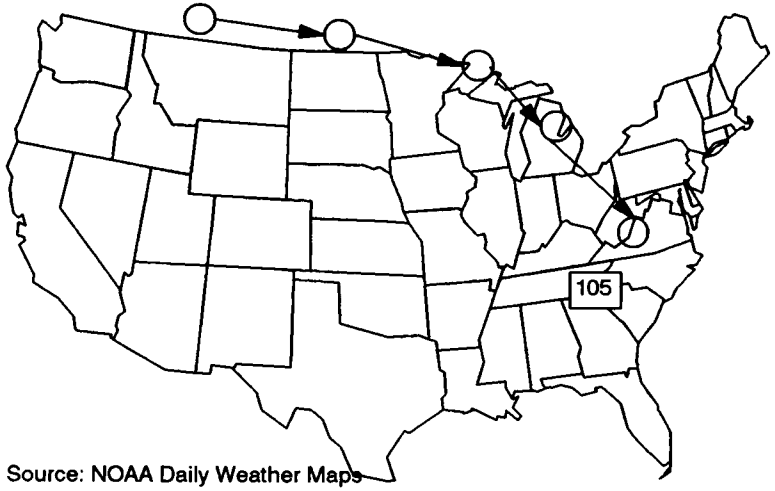
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Six Day Trajectory Ending June 12, 1990



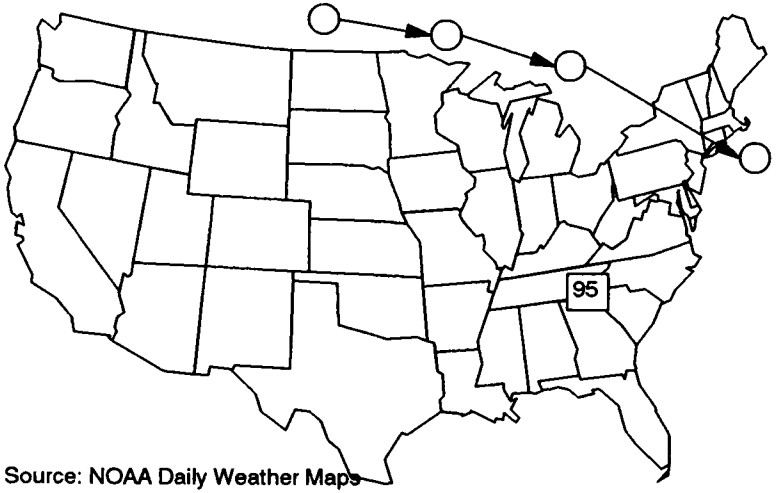
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Five Day Trajectory Ending July 3, 1990



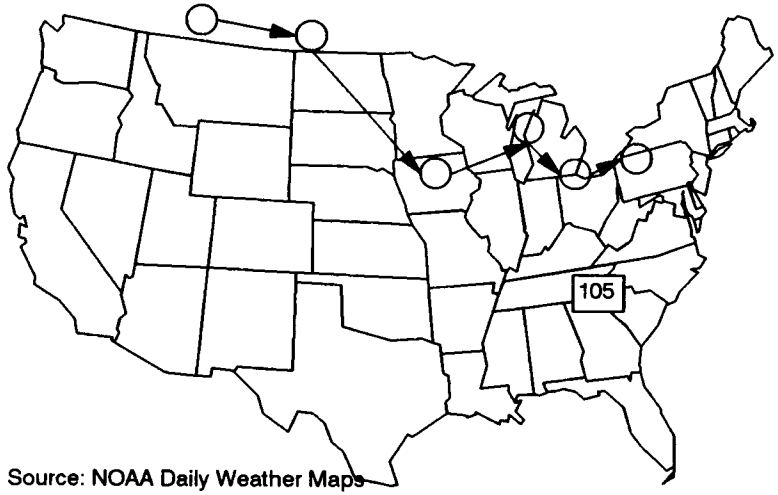
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Four Day Trajectory Ending July 8, 1990



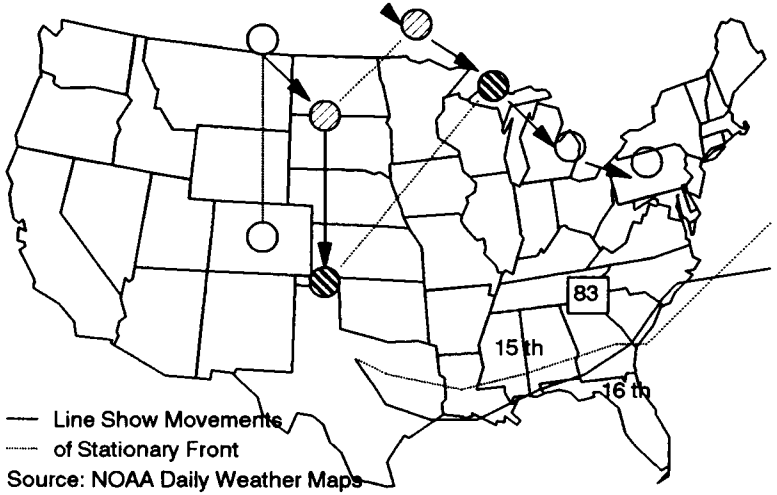
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Six Day Trajectory Ending August 3, 1990



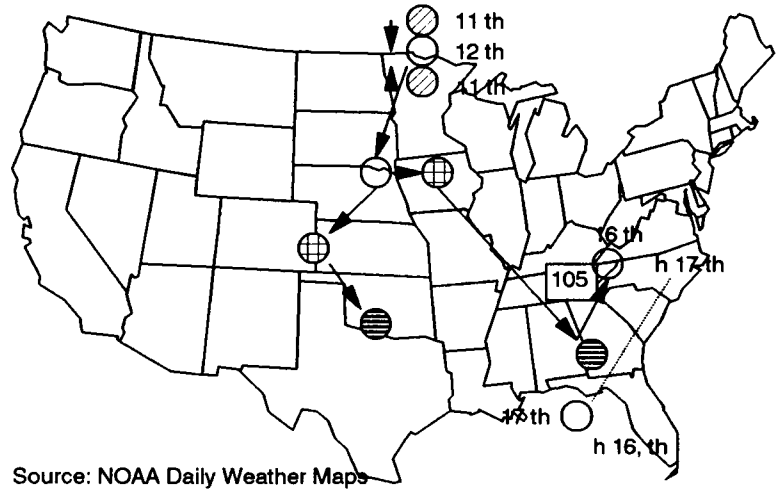
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Five Day Trajectory Ending July 16, 1991



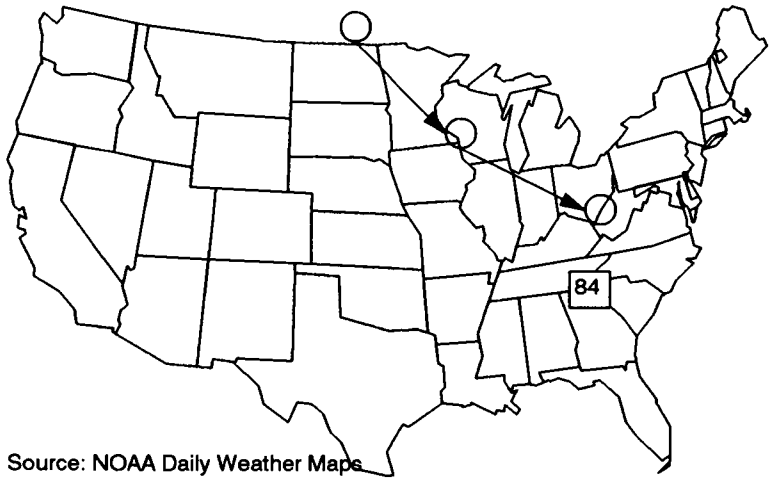
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Seven Day Trajectory Ending August 17, 1991



Source: NOAA Daily Weather Maps

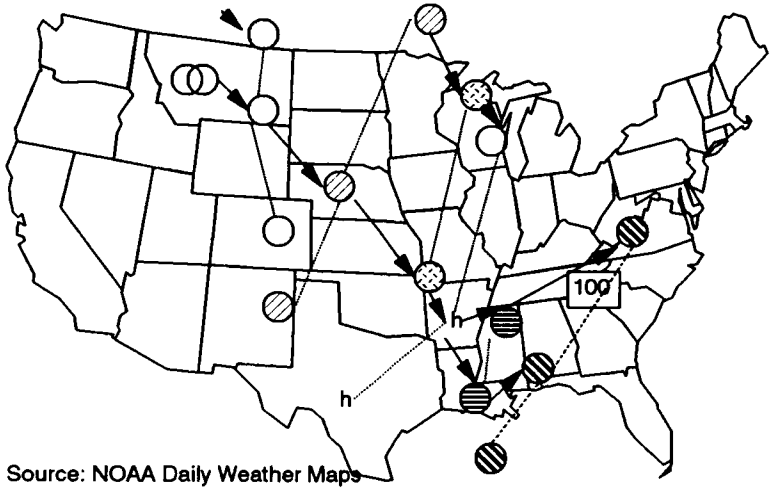
High Pressure Air Mass Impacting Air Quality in Knoxville
Three Day Trajectory Ending July 7, 1992



Source: NOAA Daily Weather Maps

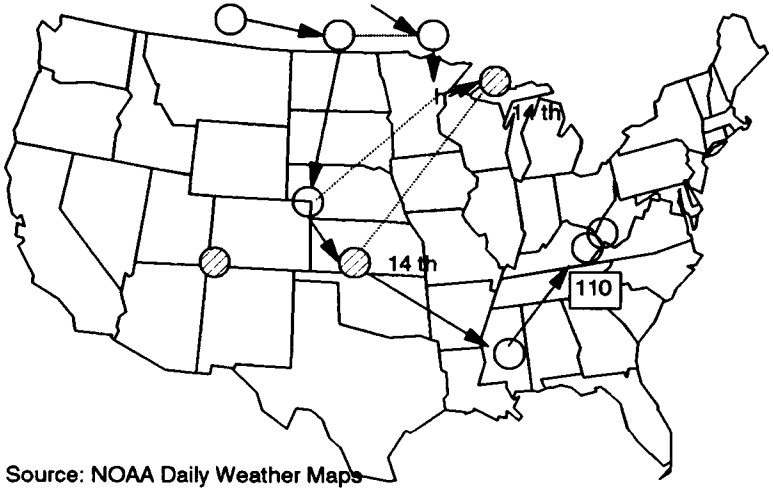
Westerner Trajectories

High Pressure Air Mass Impacting Air Quality in Knoxville
Eight Day Trajectory Ending July 25, 1988



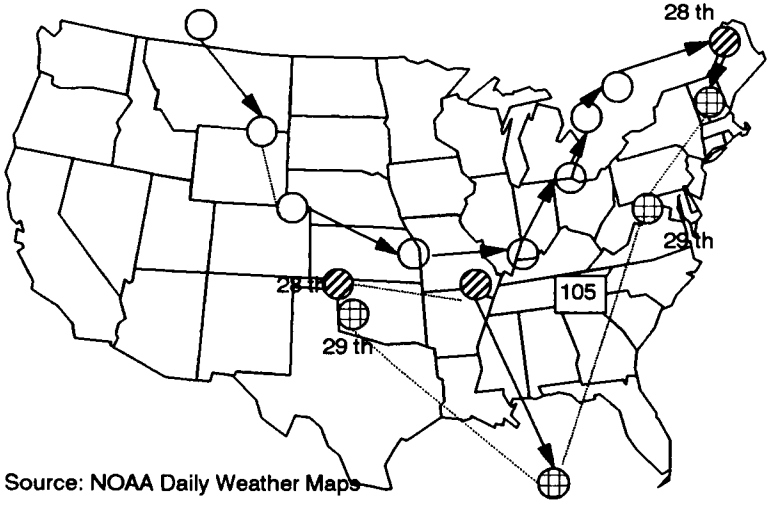
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Seven Day Trajectoy Ending July 17, 1990



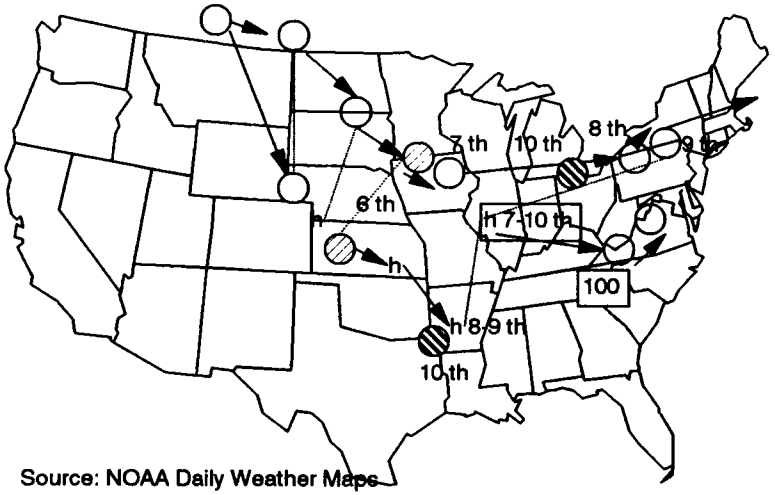
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Nine Day Trajectory Ending July 29, 1990



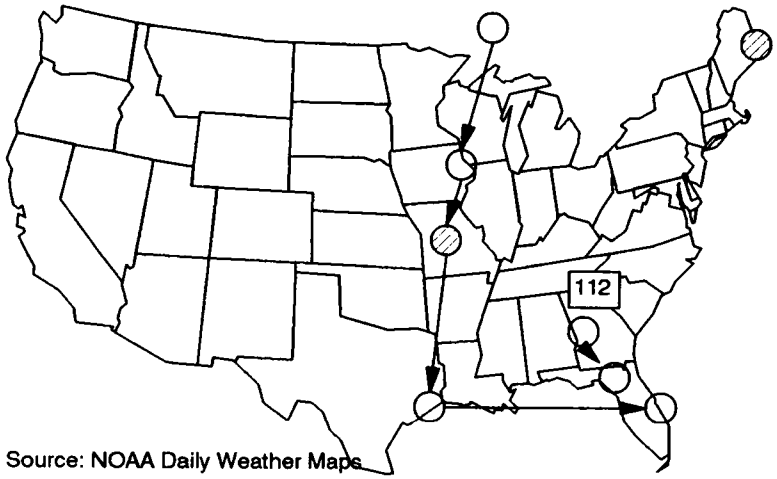
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Ten Day Trajectory Ending August 12, 1990



Source: NOAA Daily Weather Maps

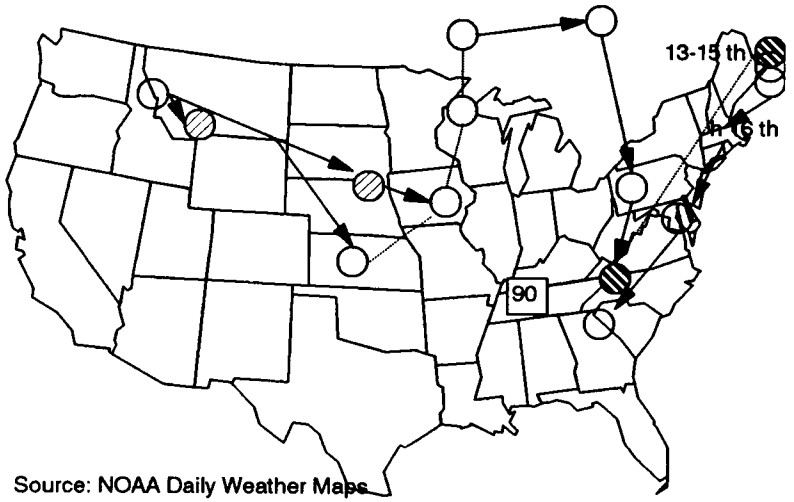
High Pressure Air Mass Impacting Air Quality in Knoxville
Seven Day Trajectory Ending May 11, 1992



Source: NOAA Daily Weather Maps

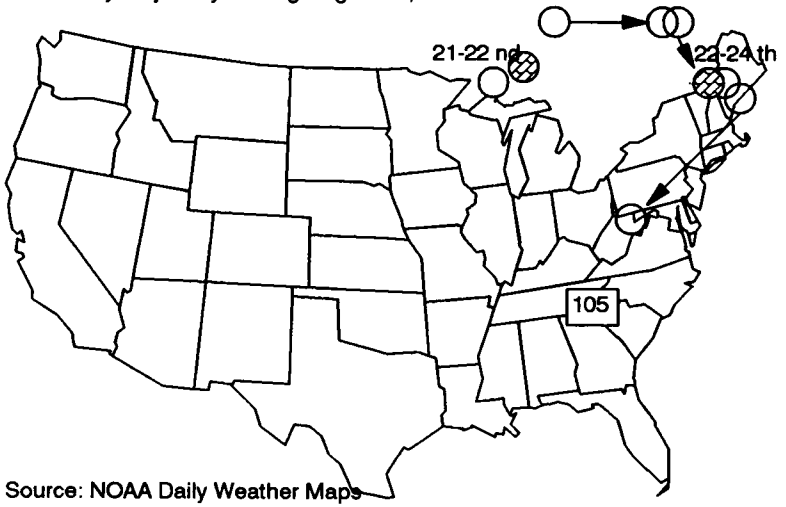
Colonist Trajectories

High Pressure Air Mass Impacting Air Quality in Knoxville
Eleven Day Trajectory Ending June 18, 1990



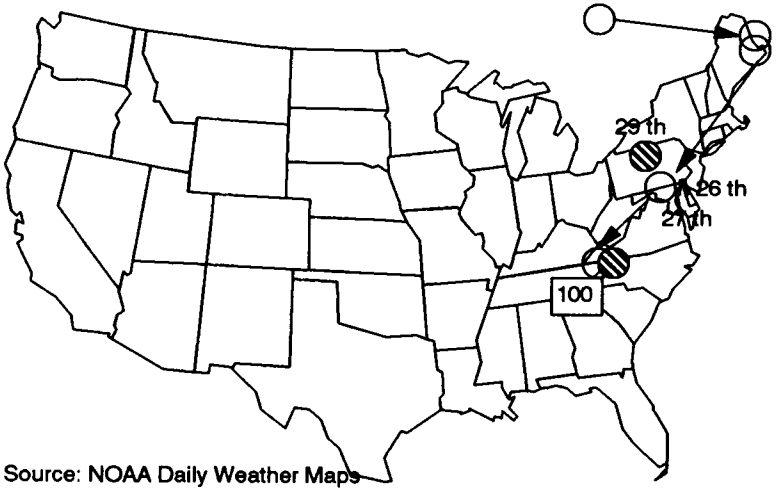
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Seven Day Trajectory Ending August 25, 1990



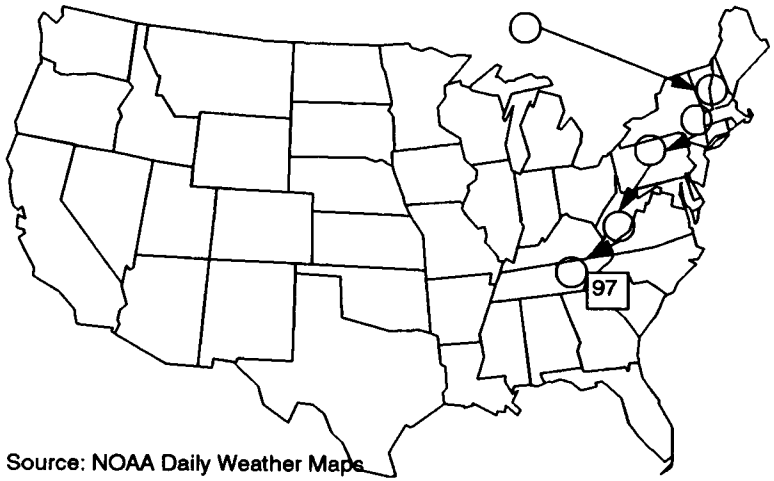
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Six Day Trajectory Ending August 29, 1991



Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Six Day Trajectory Ending May 23, 1992

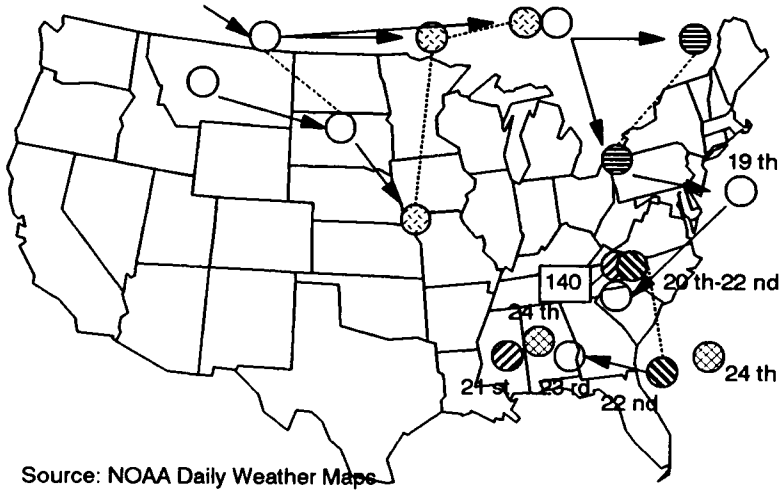


Source: NOAA Daily Weather Maps

Gulf Wanderers and Returnees Trajectories

High Pressure Air Mass Impacting Air Quality in Knoxville

Eleven Day Trajectory Ending June 24, 1988

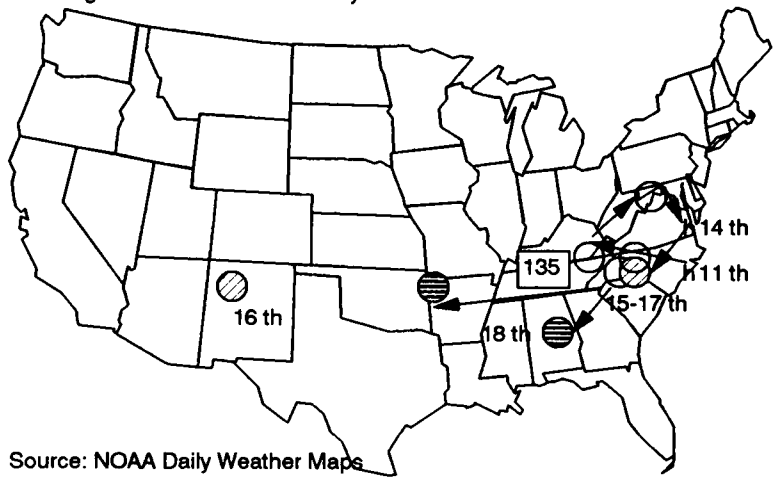


Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville

Sixteen Day Trajectory Ending August 18, 1988

See August 11 for the first nine days



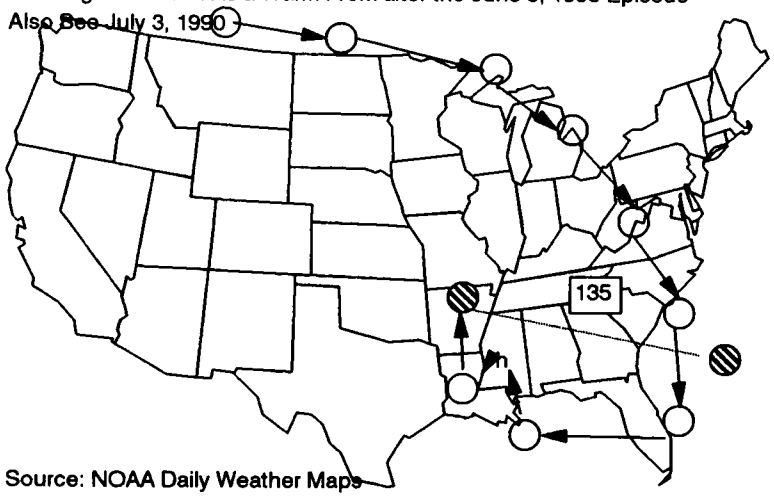
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville

Eleven Day Trajectory Ending July 9, 1990

This High Moved in As a Warm From after the June 8, 1990 Episode

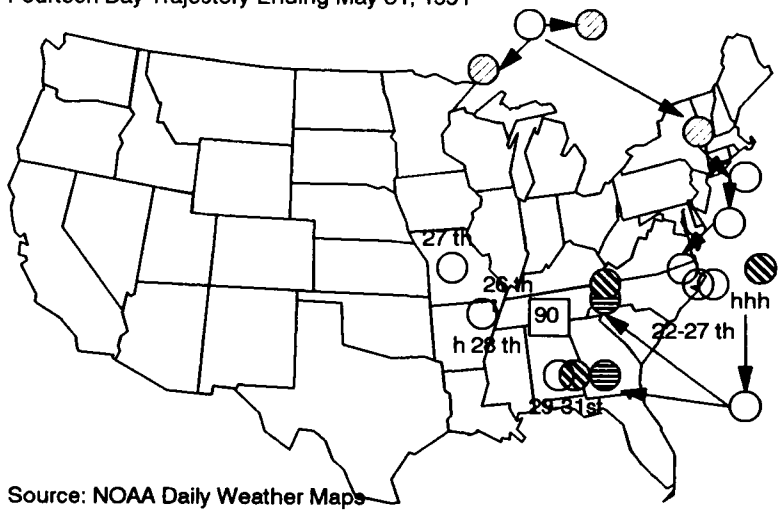
Also See July 3, 1990



Source: NOAA Daily Weather Maps

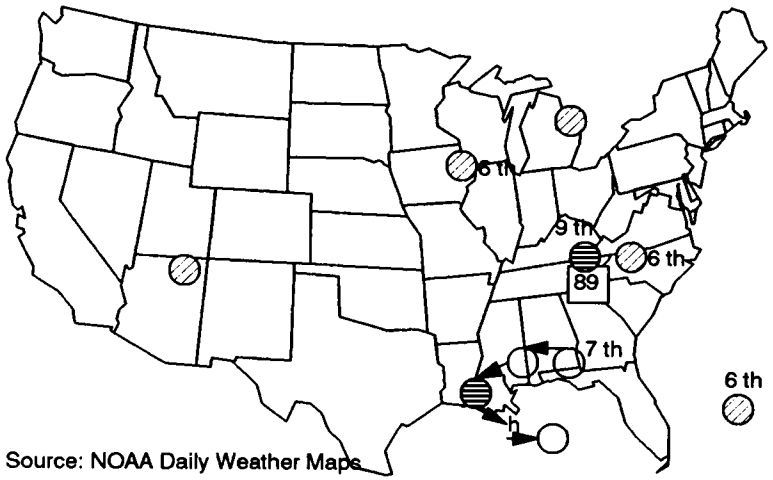
High Pressure Air Mass Impacting Air Quality in Knoxville

Fourteen Day Trajectory Ending May 31, 1991



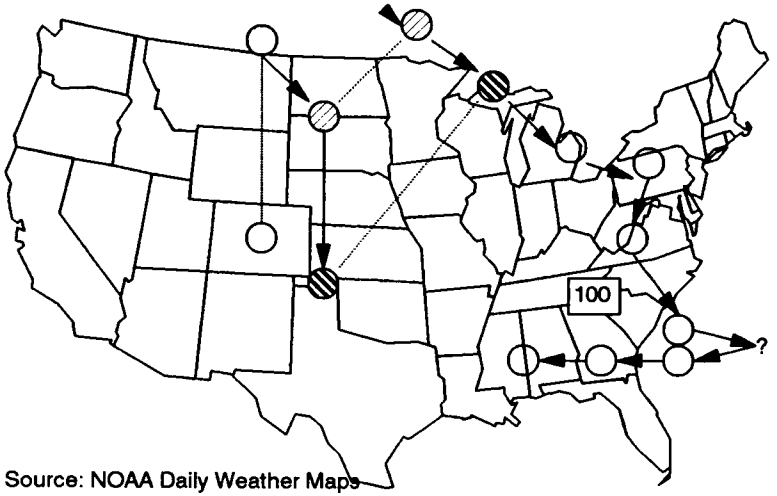
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Six Day Trajectory Ending July 11, 1991



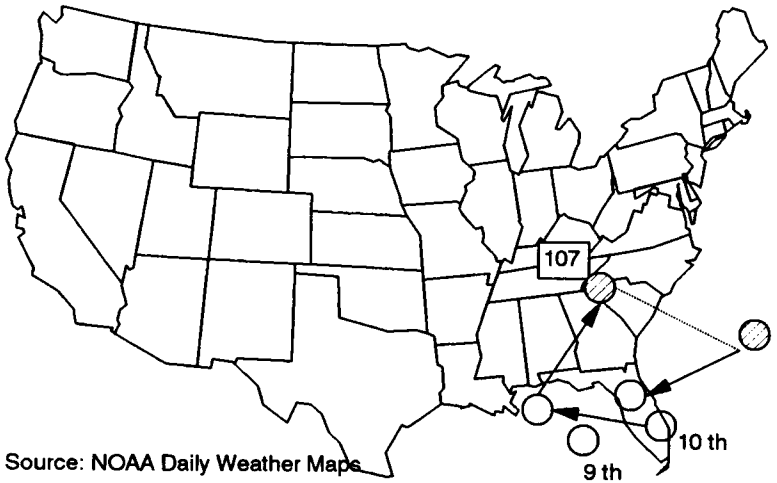
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Eleven Day Trajectory Ending July 22, 1991



Source: NOAA Daily Weather Maps

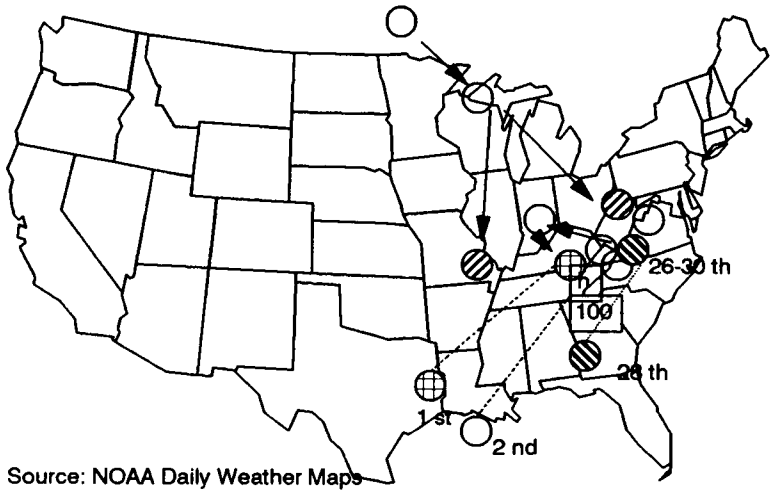
High Pressure Air Mass Impacting Air Quality in Knoxville
Five Day Trajectory Ending July 13, 1992



Source: NOAA Daily Weather Maps

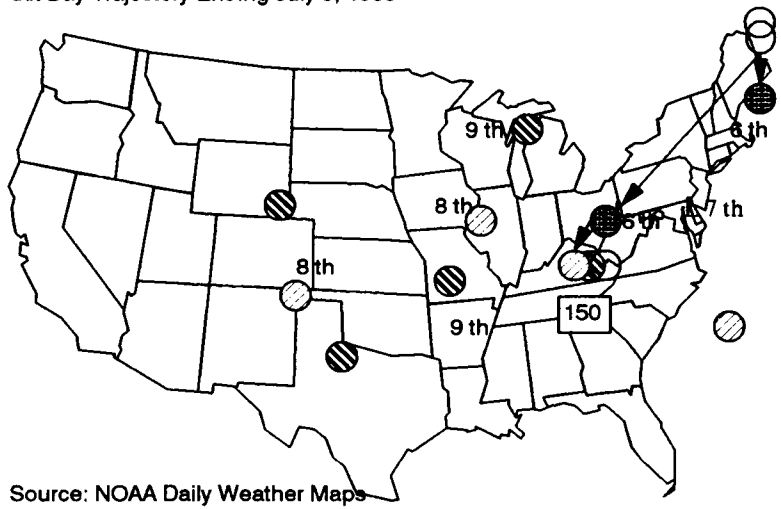
Mountain Squatter Trajectories

High Pressure Air Mass Impacting Air Quality in Knoxville
Ten Day Trajectory Ending June 2, 1988



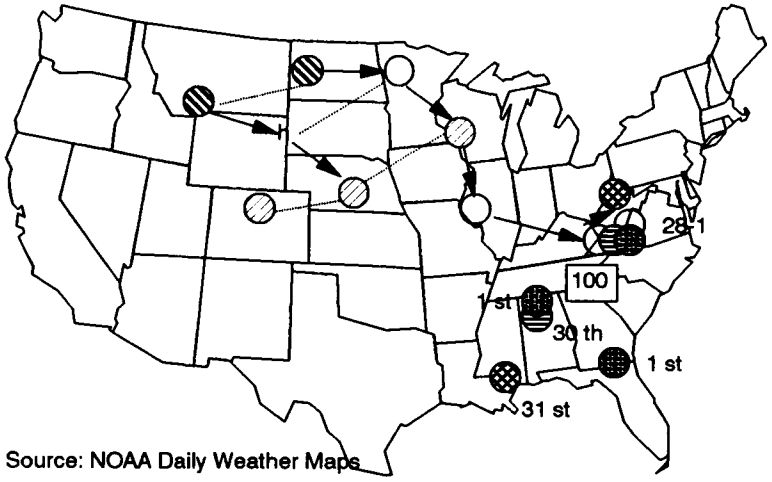
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Six Day Trajectory Ending July 9, 1988



Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Nine Day Trajectory Ending August 1, 1988



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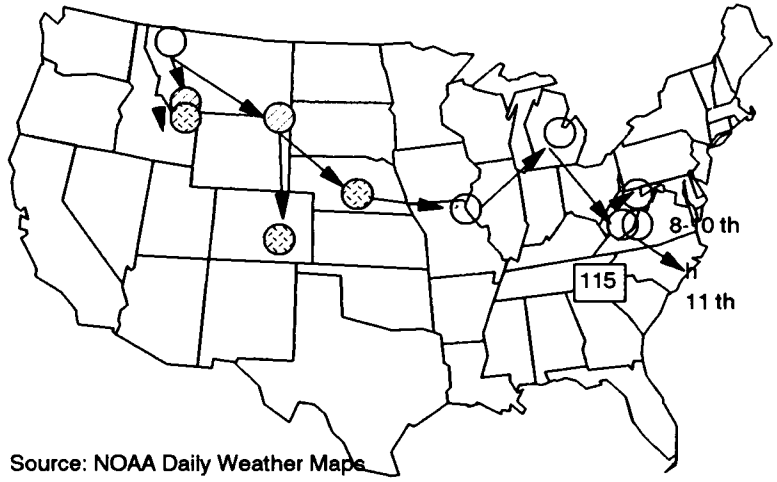
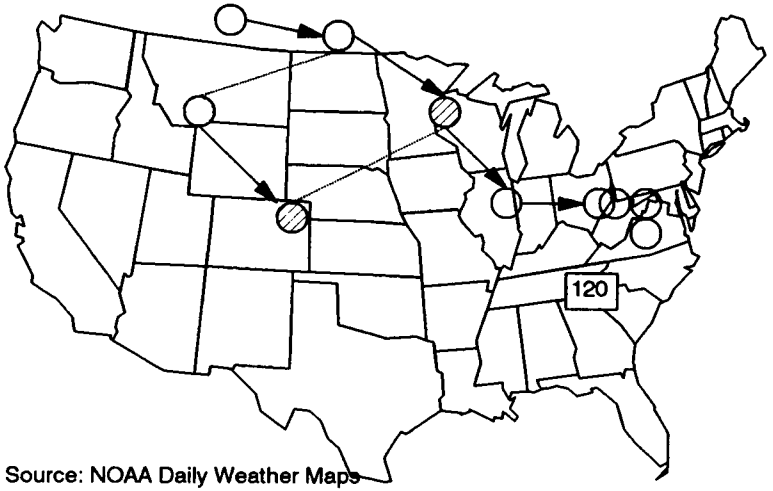
High Pressure Air Mass Impacting Air Quality in Knoxville
Nine Day Trajectory Ending August 11, 1988



Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Eight Day Trajectory Ending August 18, 1990



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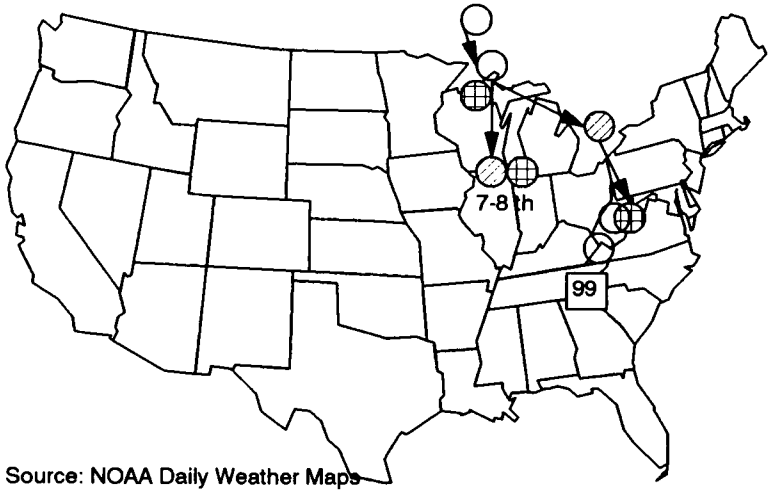
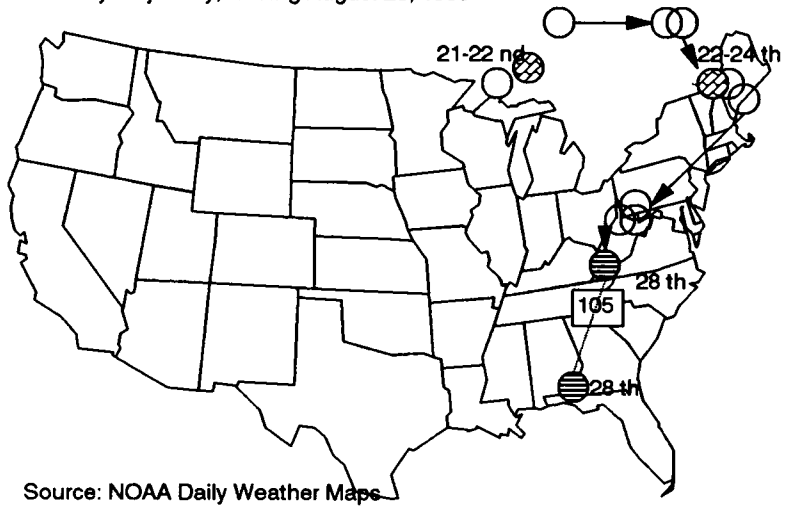
High Pressure Air Mass Impacting Air Quality in Knoxville
Six Day Trajectory Ending June 10, 1991



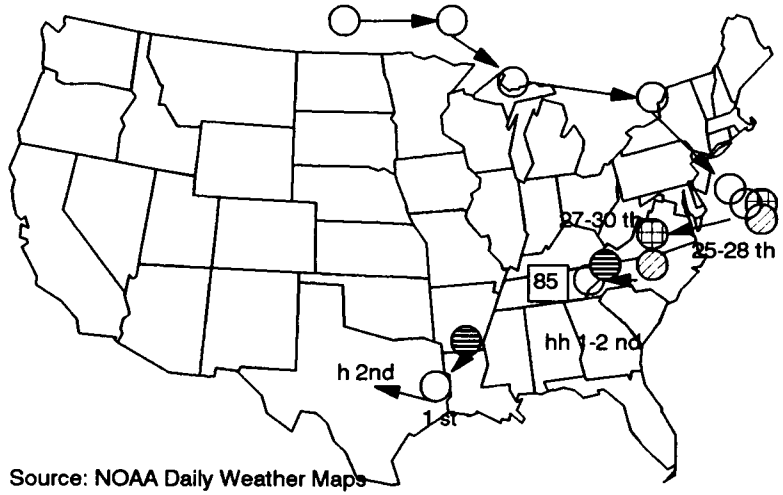
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Ten Day Trajectory, Ending August 28, 1990



Source: NOAA Daily Weather Maps

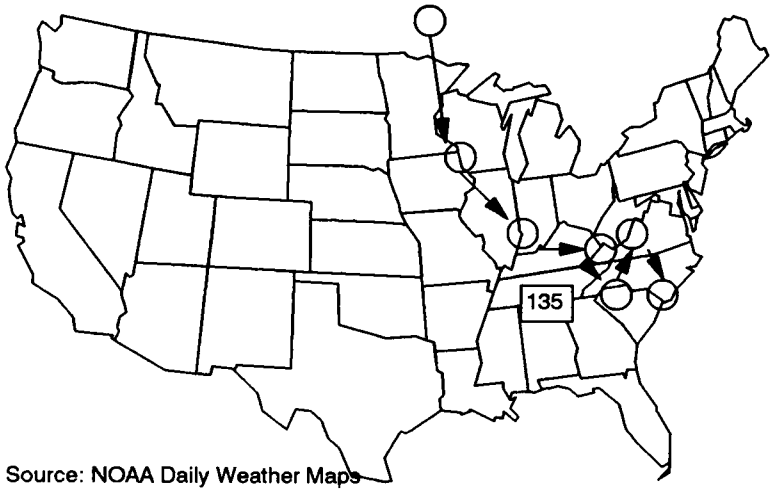
High Pressure Air Mass Impacting Air Quality in Knoxville
Twelve Day Trajectory Ending July 2, 1991



Source: NOAA Daily Weather Maps

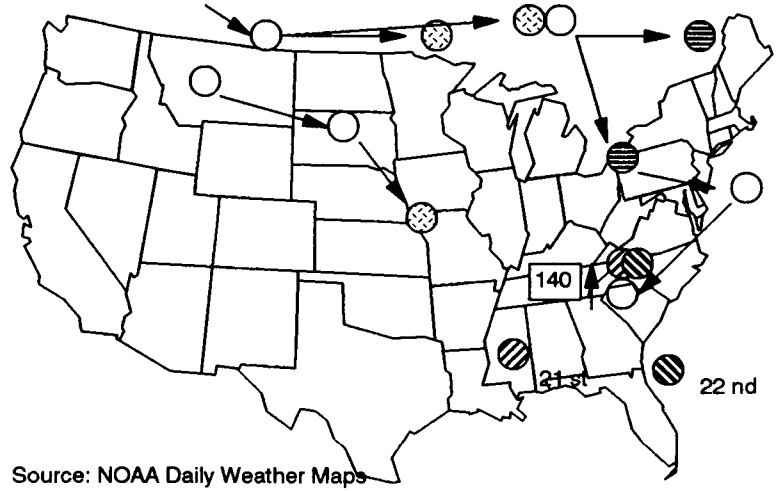
Coastal Squatter Trajectories

High Pressure Air Mass Impacting Air Quality in Knoxville
Seven Day Trajectory Ending June 15, 1988



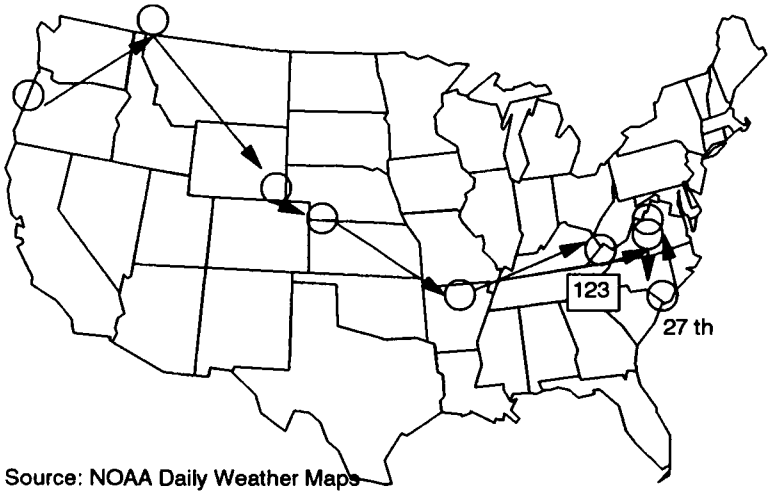
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Ten Day Trajectory Ending June 22, 1988



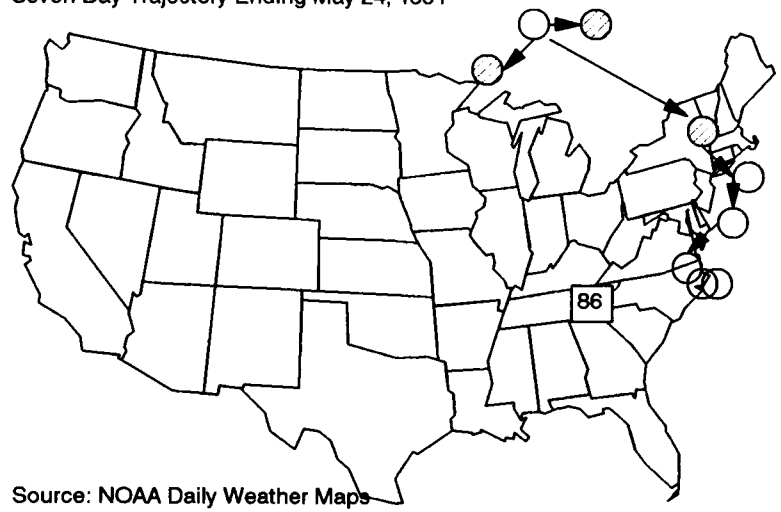
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Nine Day Trajectory Ending June 28, 1990



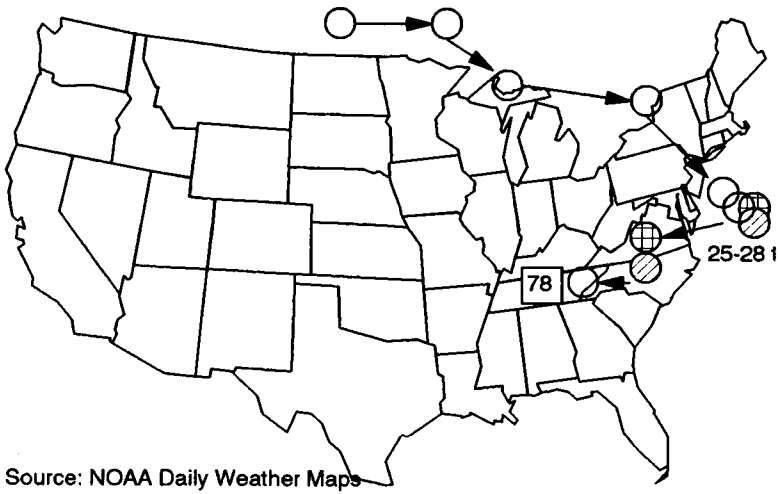
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Seven Day Trajectory Ending May 24, 1991



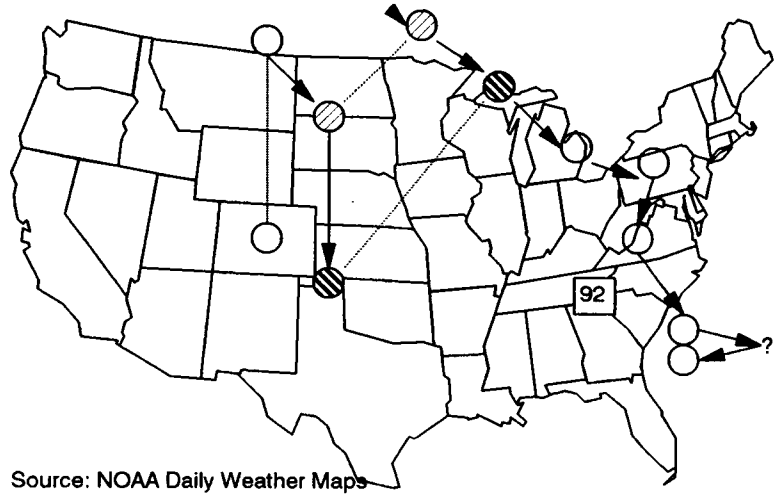
Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Nine Day Trajectory Ending June 29, 1991



Source: NOAA Daily Weather Maps

High Pressure Air Mass Impacting Air Quality in Knoxville
Nine Day Trajectory Ending July 20, 1991

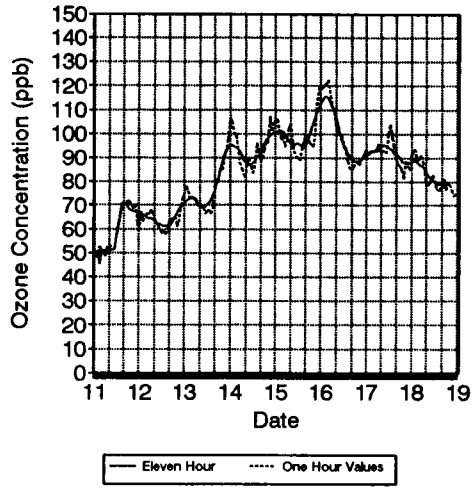


Source: NOAA Daily Weather Maps

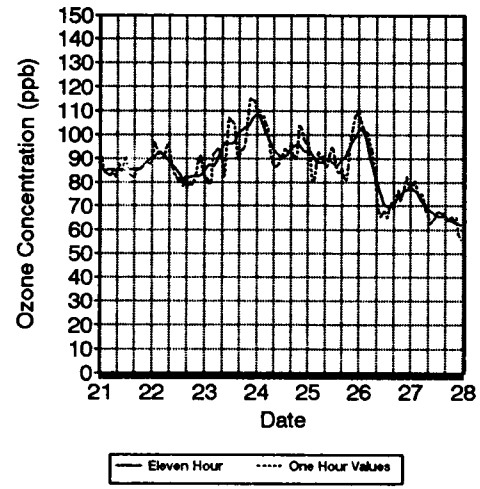
APPENDIX B

Ozone Concentrations at Specific Monitors for June 11-18, 1988; June 21-27, 1988; and July 4-11, 1988

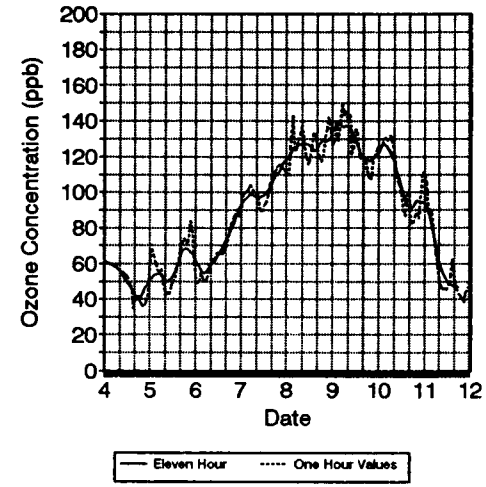
Mount Mitchell Ozone, With and Without Eleven Hour Dampening, June 11-18, 1988



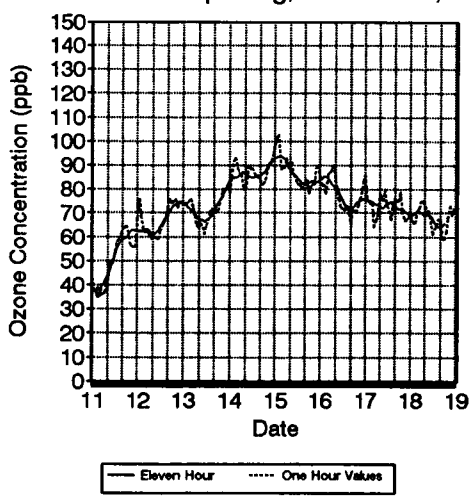
Mount Mitchell Ozone, With and Without Eleven Hour Dampening, June 21-27, 1988



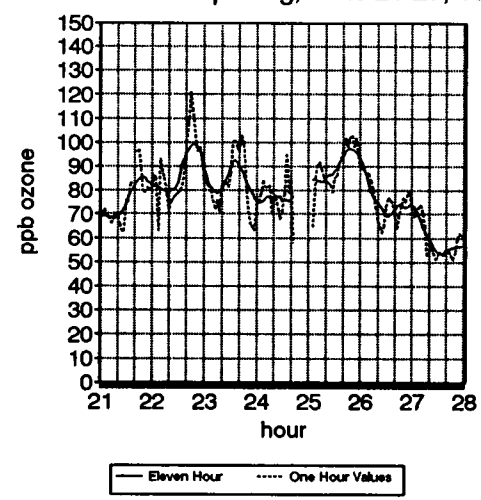
Mount Mitchell Ozone, With and Without Eleven Hour Dampening, July 4-11, 1988



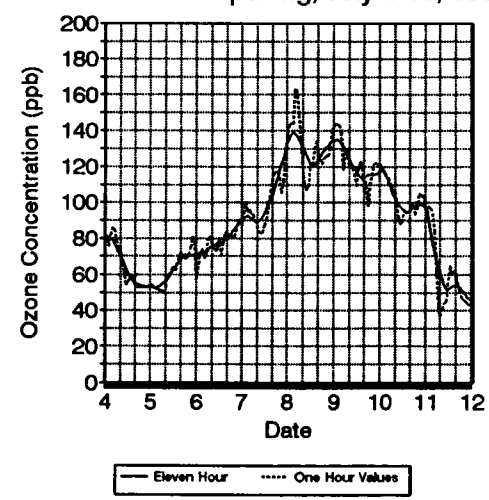
White Top Ozone, With and Without Eleven Hour Dampening, June 11-18, 1988



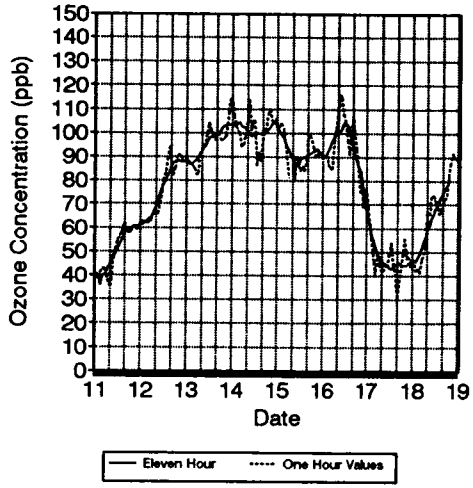
White Top Ozone, With and Without Eleven Hour Dampening, June 21-27, 1988



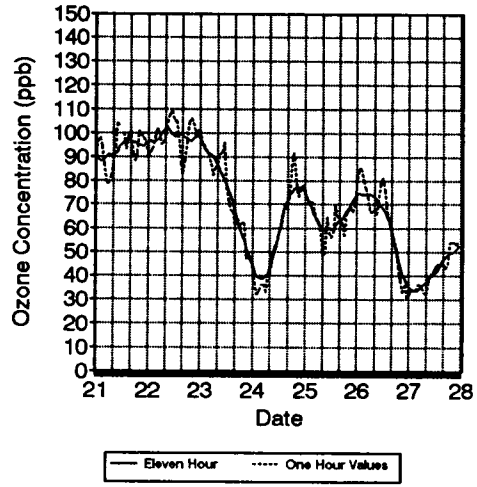
White Top Ozone, With and Without Eleven Hour Dampening, July 4-11, 1988



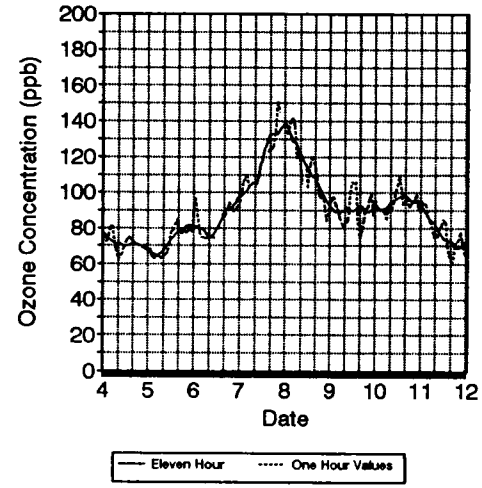
Dickey Ridge Ozone, With and Without Eleven Hour Dampening, June 11-18, 1988



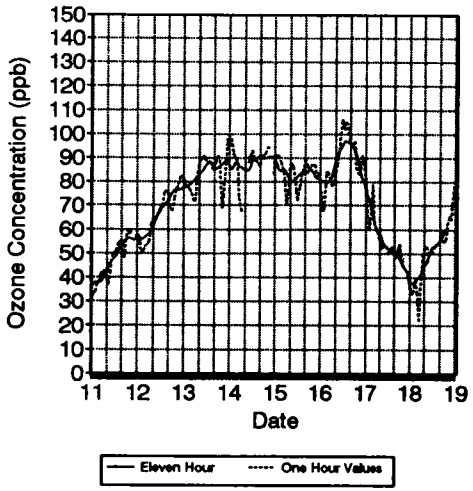
Dickey Ridge Ozone, With and Without Eleven Hour Averages, June 21-27, 1988



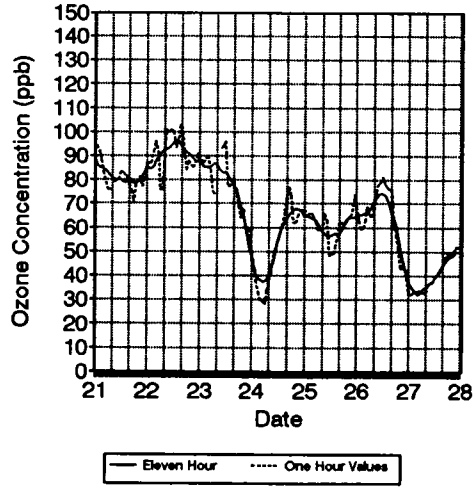
Dickey Ridge Ozone, With and Without Eleven Hour Dampening, July 4-11, 1988



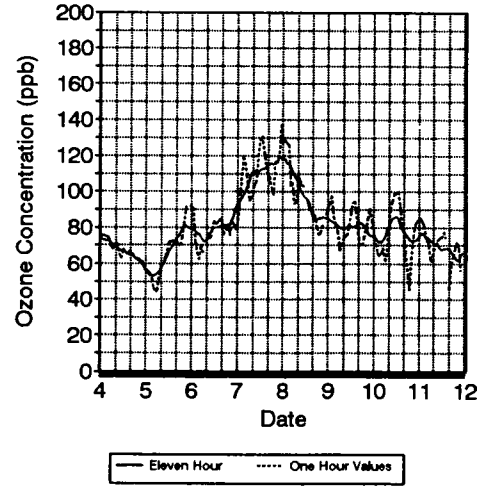
Big Meadows Ozone, With and Without Eleven Hour Dampening, June 11-18, 1988



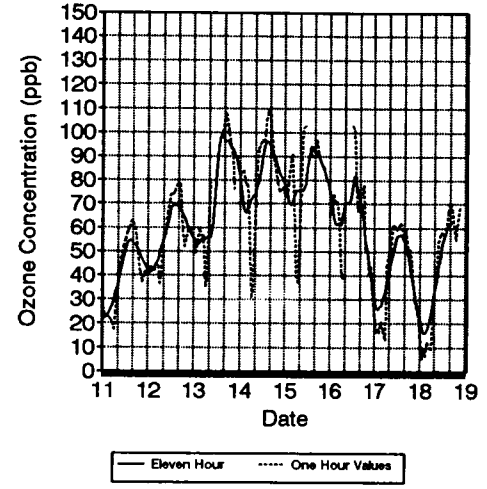
Big Meadows Ozone, With and Without Eleven Hour Dampening, June 21-27, 1988



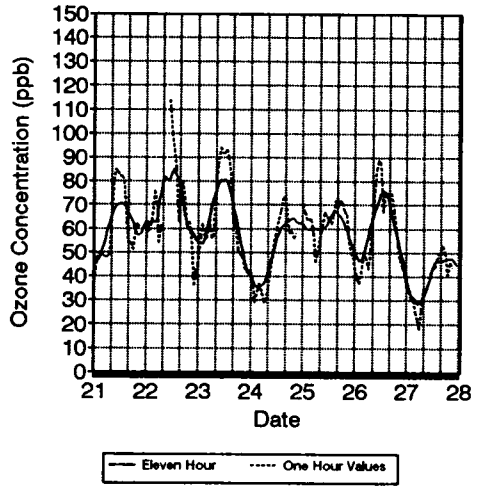
Big Meadows Ozone, With and Without Eleven Hour Dampening, July 4-11, 1988



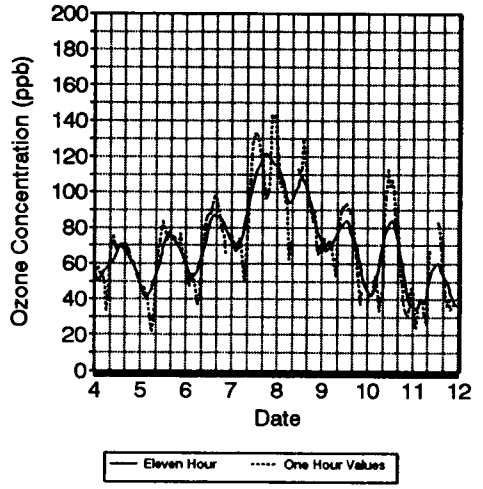
Saw Mill Run Ozone, With and Without Eleven Hour Dampening, June 11-18, 1988



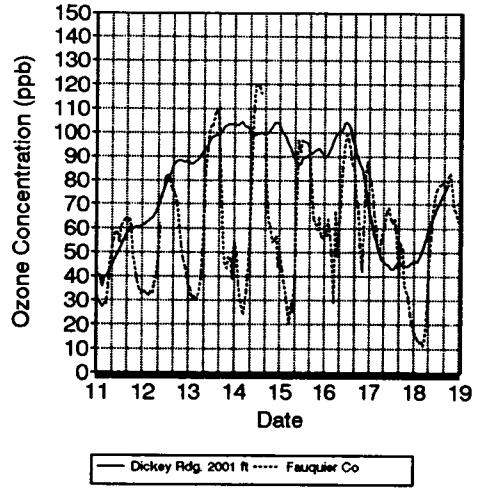
Saw Mill Run Ozone, With and Without Eleven Hour Dampening, June 21-27, 1988



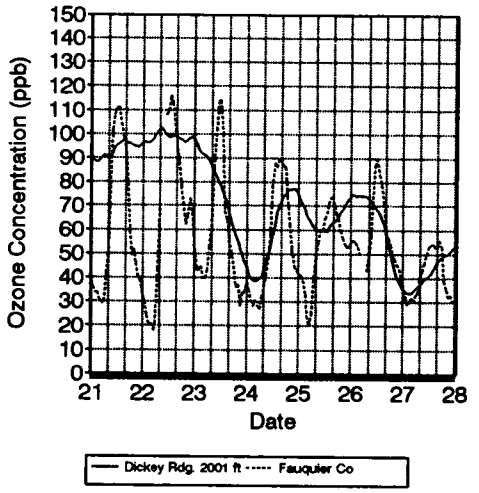
Saw Mill Run Ozone, With and Without Eleven Hour Dampening, July 4-11, 1988



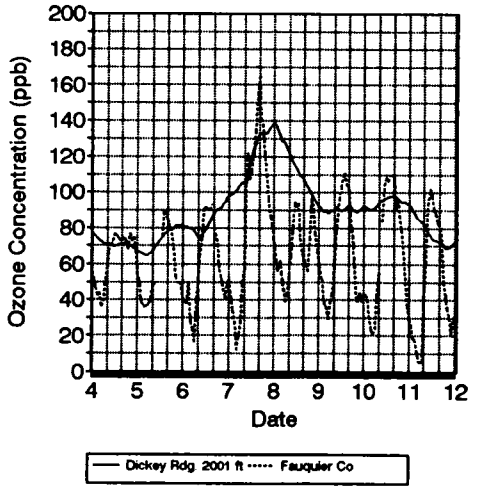
Ozone Aloft With Eleven Hour Dampening, and Fauquier Co., Va, June 11-18, 1988



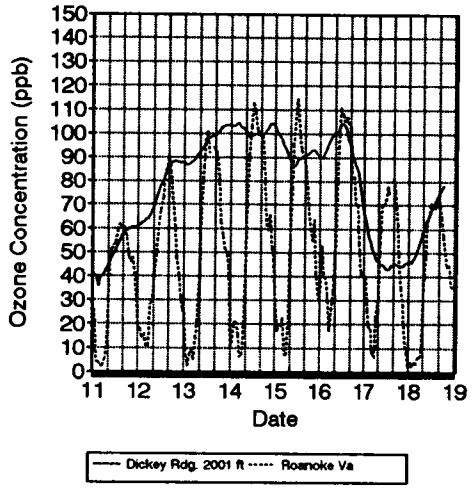
Ozone Aloft, Eleven Hour Dampening, and Fauquier Co., Va, June 21-27, 1988



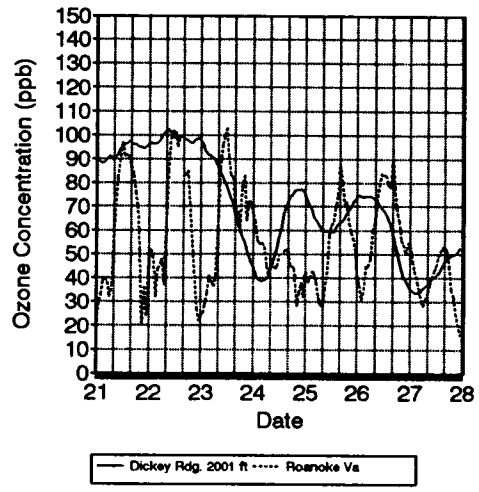
Ozone Aloft With Eleven Hour Dampening, and Fauquier Co., Va, July 4-11, 1988



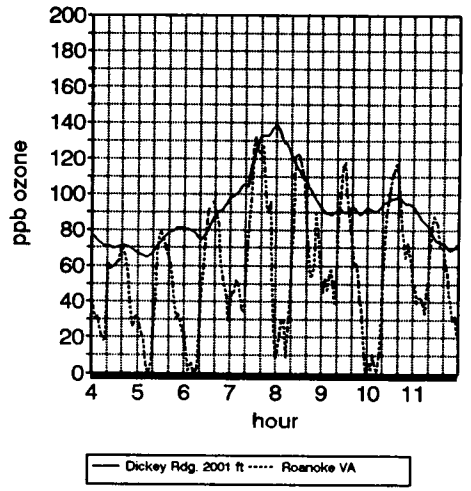
Ozone Aloft With Eleven Hour Dampening, and Roanoke, Va, June 11-18, 1988



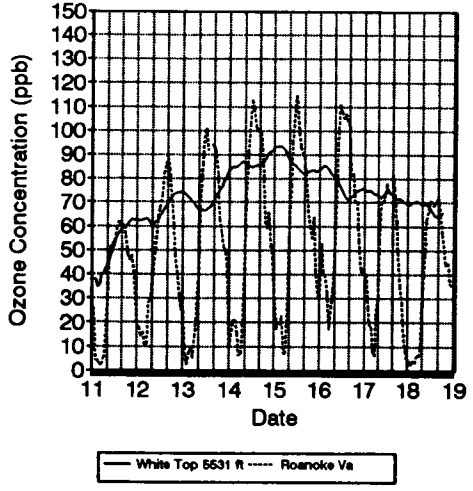
Ozone Aloft With Eleven Hour Dampening, and Roanoke, Va, June 21-27, 1988



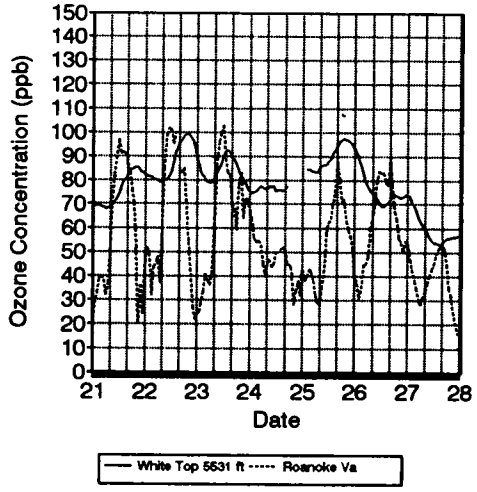
Ozone Aloft, Eleven Hour Dampening, and Roanoke, Va, July 4-11, 1988



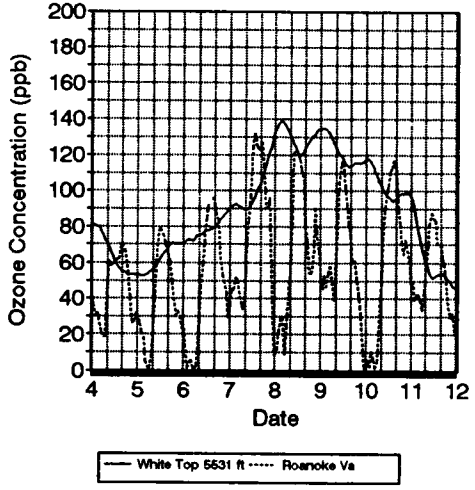
Ozone Aloft With Eleven Hour Dampening, and Roanoke, Va, June 11-18, 1988



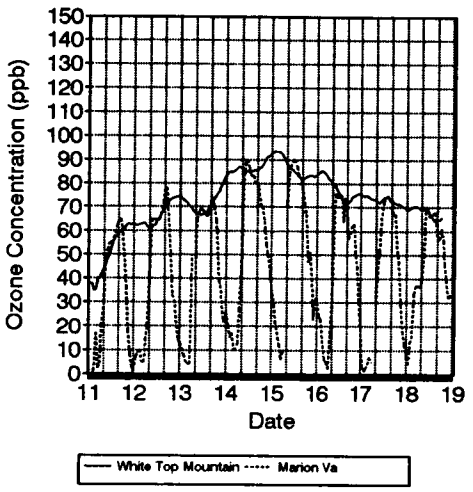
Ozone Aloft With Eleven Hour Dampening, and Roanoke, Va, June 21-27, 1988



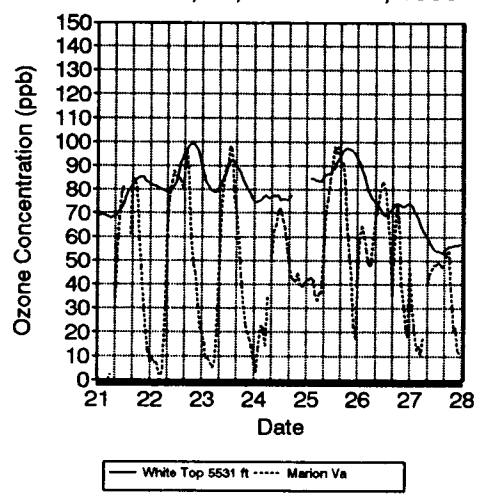
Ozone Aloft With Eleven Hour Dampening, and Roanoke, Va, July 4-11, 1988



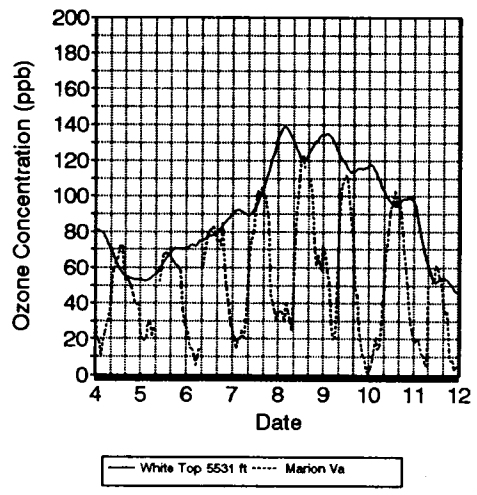
Ozone Aloft With Eleven Hour Dampening, and Marion, Va, June 11-18, 1988



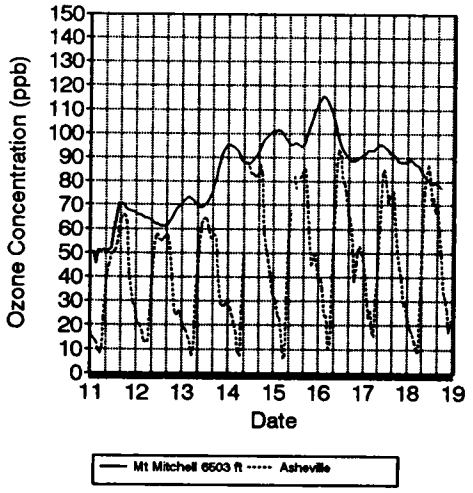
Ozone Aloft With Eleven Hour Dampening, and Marion, Va, June 21-27, 1988



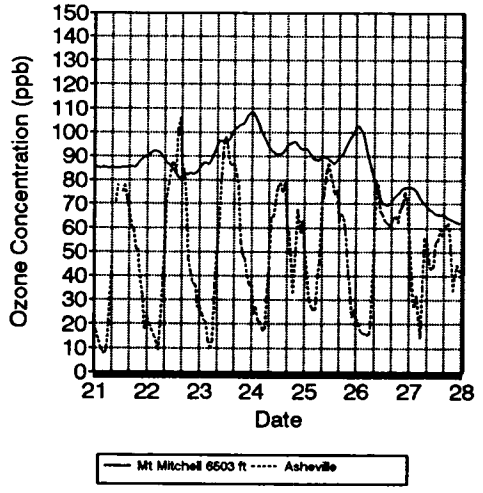
Ozone Aloft With Eleven Hour Dampening, and Marion, Va, July 4-11, 1988



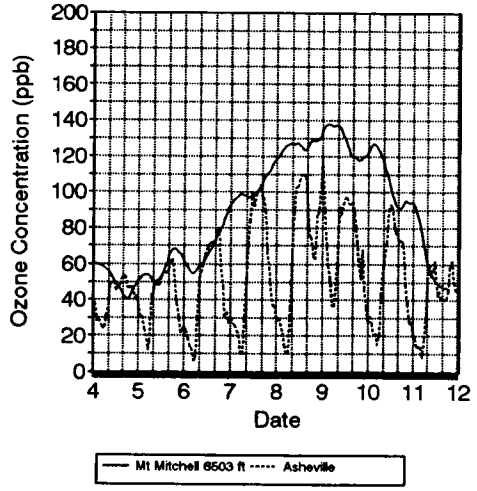
Ozone Aloft With Eleven Hour Dampening, and Asheville, NC, June 11-18, 1988



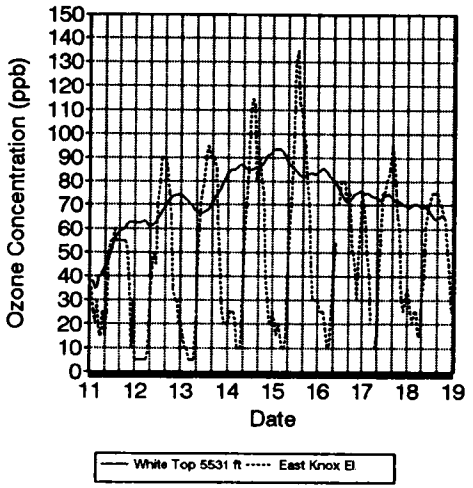
Ozone Aloft With Eleven Hour Dampening, and Asheville, NC, June 21-27, 1988



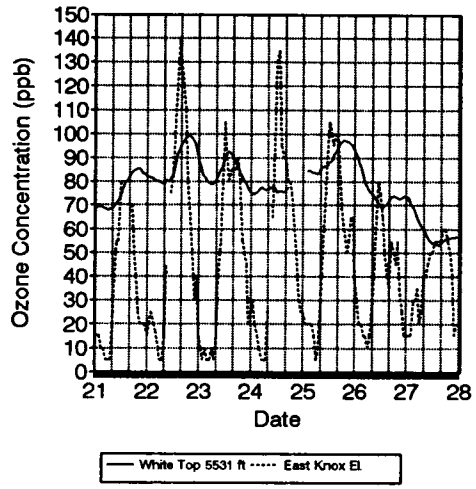
Ozone Aloft, Eleven Hour Dampening, and Asheville, NC, July 4-11, 1988



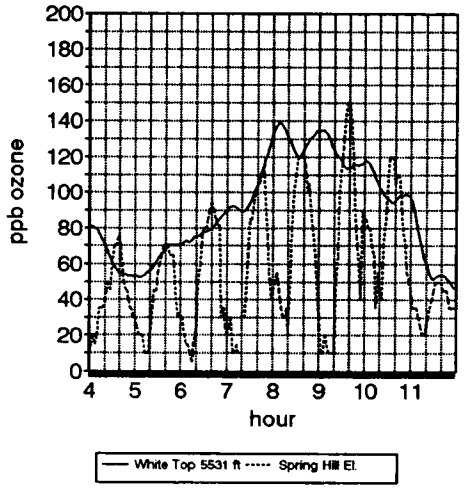
Ozone Aloft With Eleven Hour Dampening, and Knoxville, Tn, June 11-18, 1988



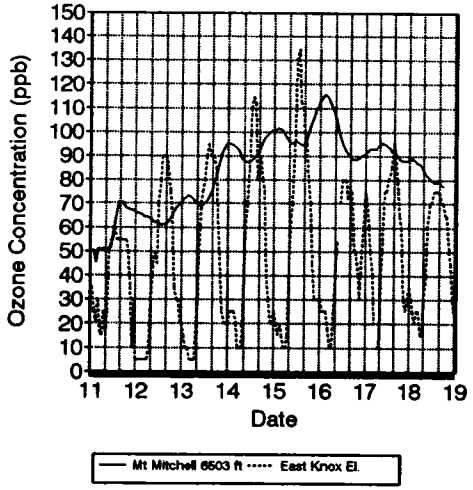
Ozone Aloft With Eleven Hour Dampening, and Knoxville, Tn, June 21-27, 1988



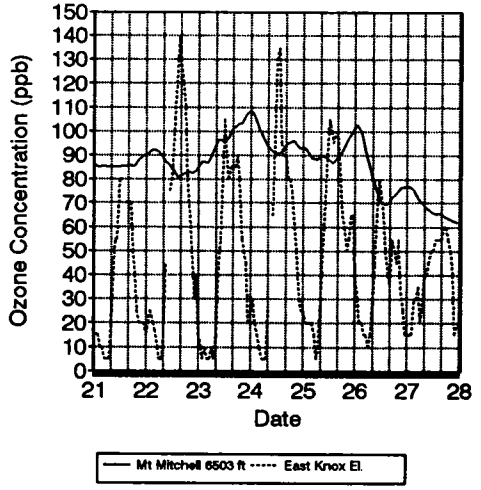
Ozone Aloft, Eleven Hour Dampening, and Knoville, Tn, July 4-11, 1988



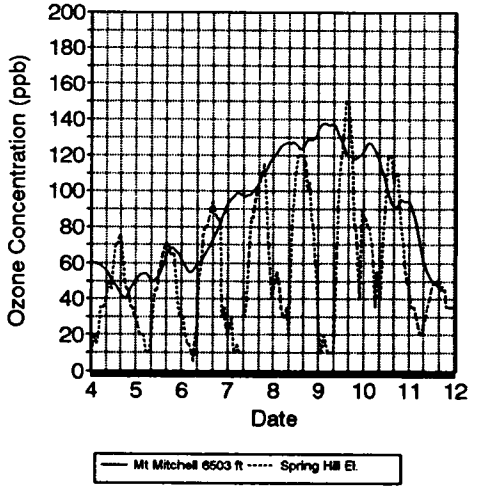
Ozone Aloft With Eleven Hour Dampening, and Knoxville, Tn, June 11-18, 1988



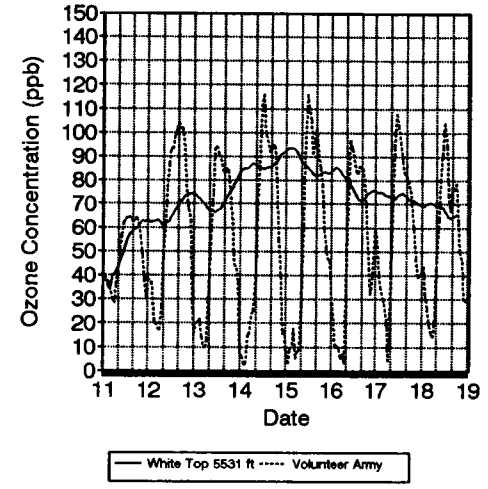
Ozone Aloft With Eleven Hour Dampening, and Knoxville, Tn, June 21-27, 1988



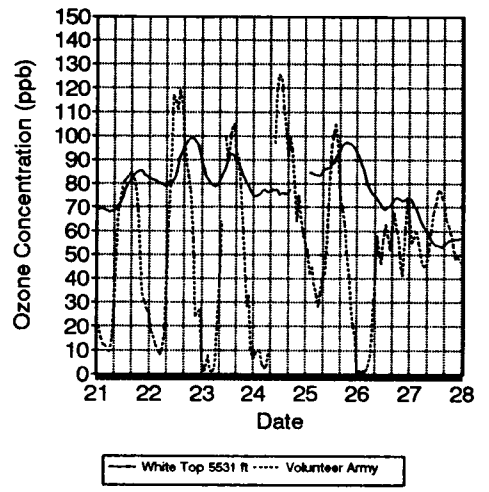
Ozone Aloft, Eleven Hour Dampening, and Knoville, Tn, July 4-11, 1988



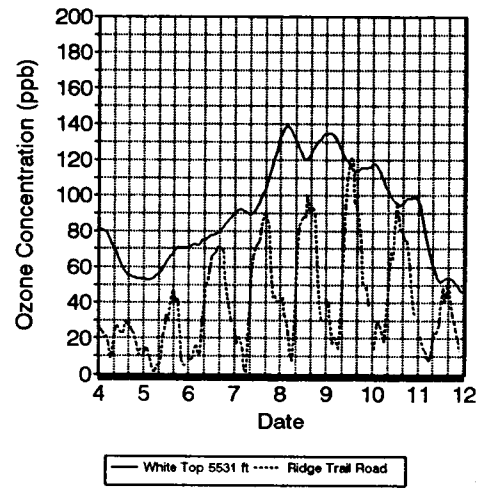
Ozone Aloft With Eleven Hour Dampening, and Chattanooga, Tn, June 11-18, 1988



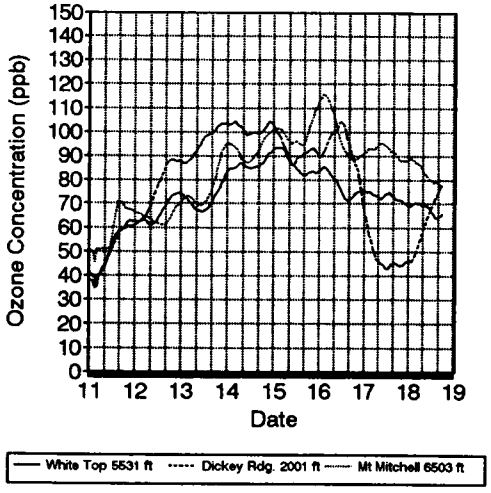
Ozone Aloft With Eleven Hour Dampening, and Chattanooga, Tn, June 21-27, 1988



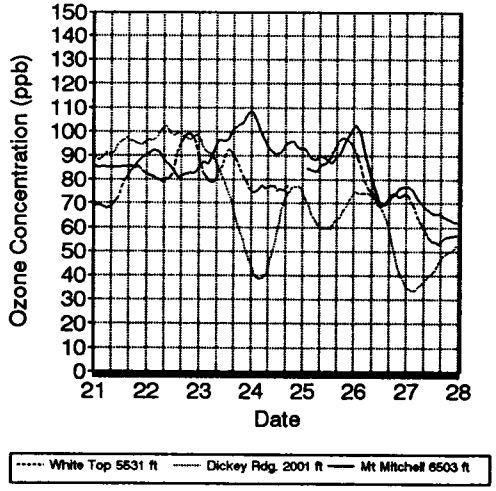
Ozone Aloft With Eleven Hour Dampening, and Chattanooga, Tn, July 4-11, 1988



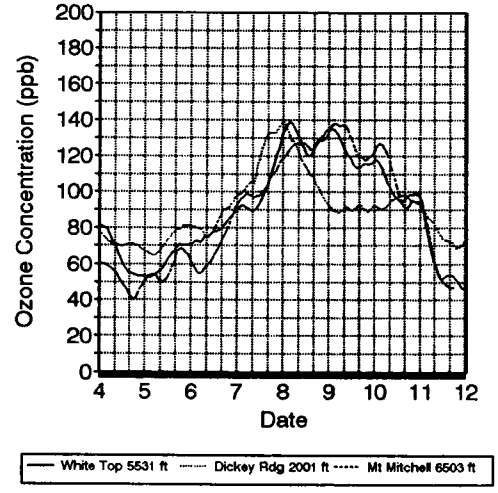
Ozone Aloft, Eleven Hour Dampening June 11-18, 1988



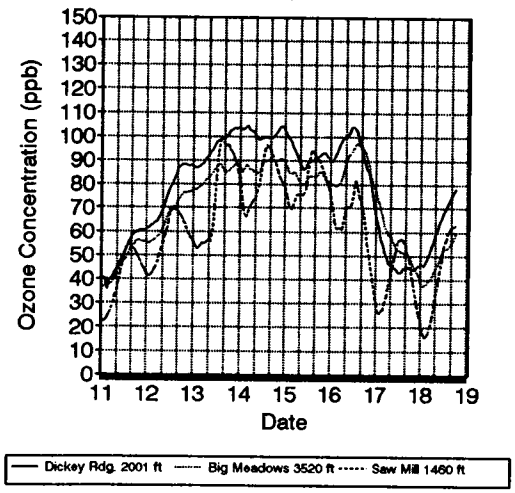
Ozone Aloft, Eleven Hour Dampening June 21-27, 1988



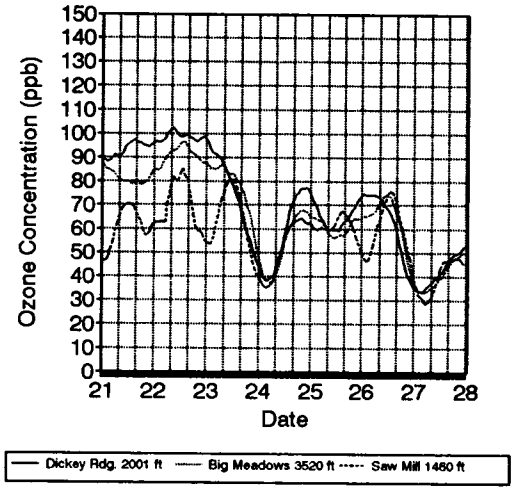
Ozone Aloft, Eleven Hour Dampening July 4-11, 1988



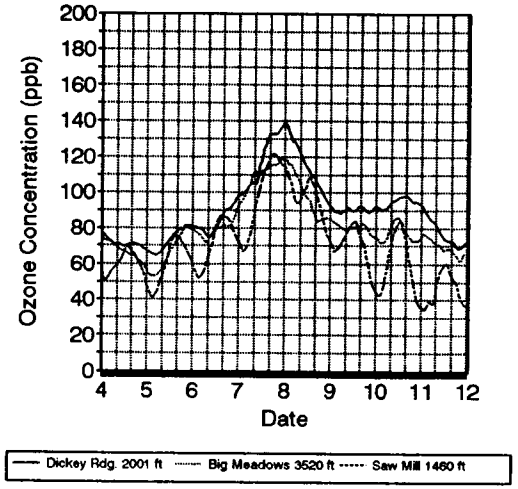
Shenandoah National Park Ozone With Eleven Hour Dampening, June 11-18, 1988



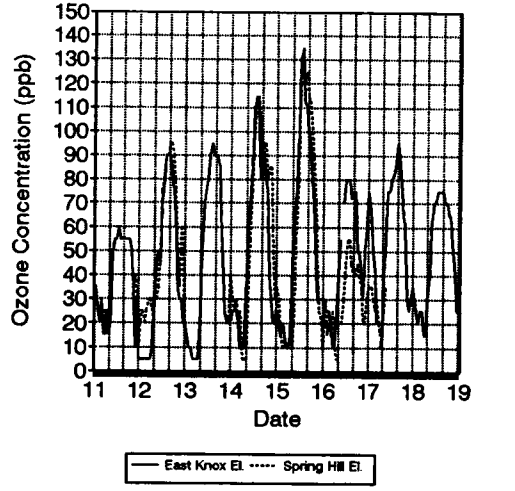
Shenandoah National Park Ozone With Eleven Hour Dampening, June 21-27, 1988



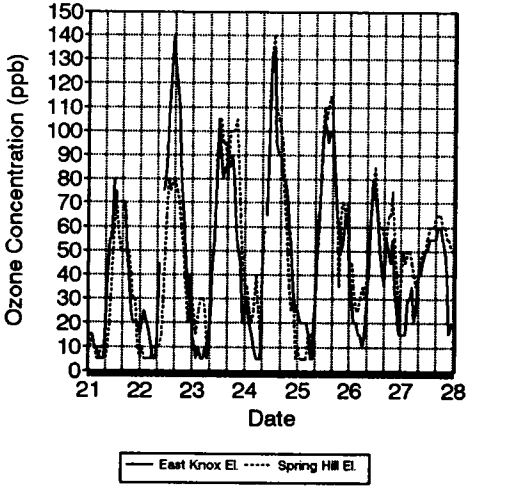
Shenandoah National Park Ozone With Eleven Hour Dampening, July 4-11, 1988



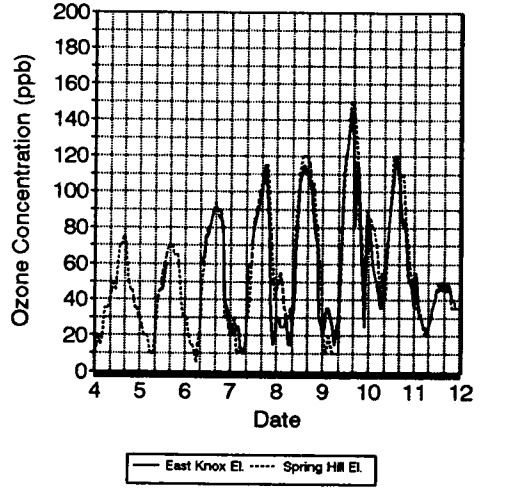
Hourly, Ozone Concentrations Knoxville, Tn, June 11-18, 1988



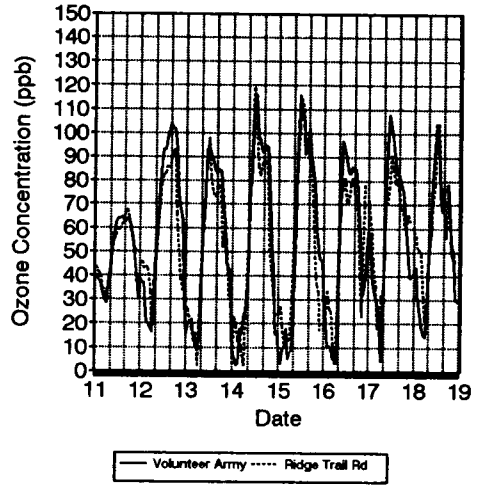
Hourly Ozone Concentrations Knoxville, Tn, June 21-27, 1988



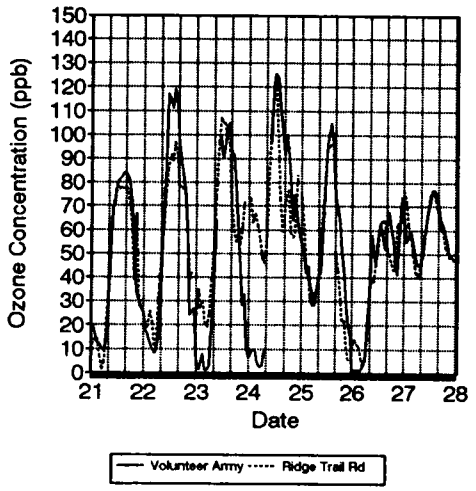
Hourly Ozone Concentrations Knoxville, Tn, July 4-11, 1988



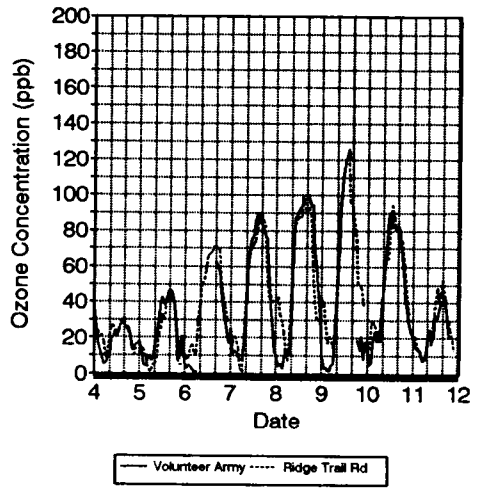
Hourly Ozone Concentrations
Chattanooga, Tn, June 11-18, 1988



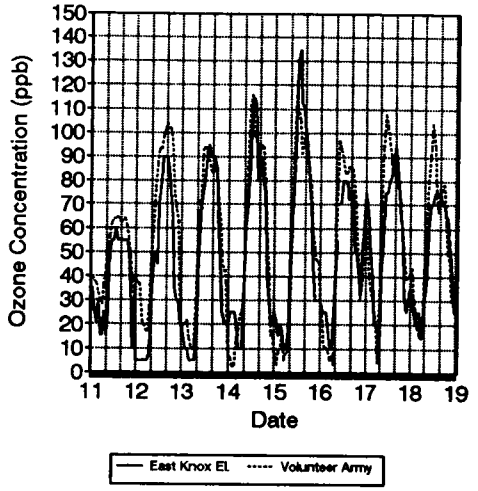
Hourly Ozone Concentrations
Chattanooga, Tn, June 21-27, 1988



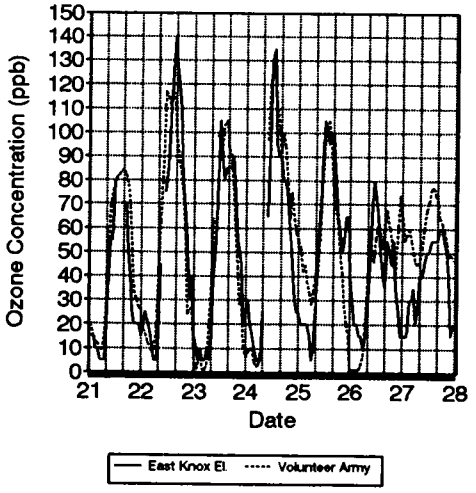
Hourly Ozone Concentrations
Chattanooga, Tn, July 4-11, 1988



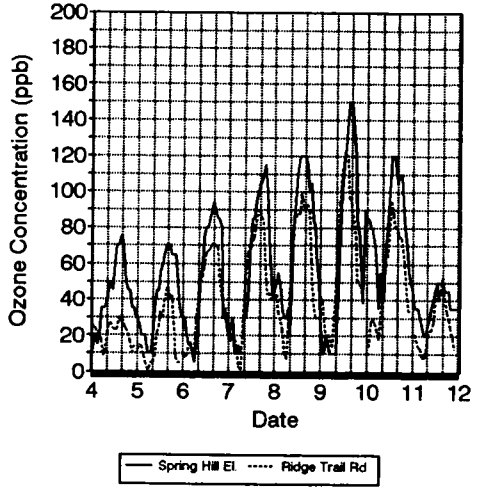
Hourly Ozone Concentrations in East
Tennessee, June 11-18, 1988



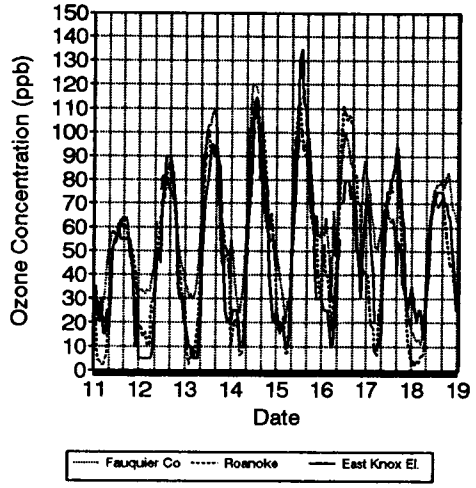
Hourly Ozone Concentrations in East
Tennessee, June 21-27, 1988



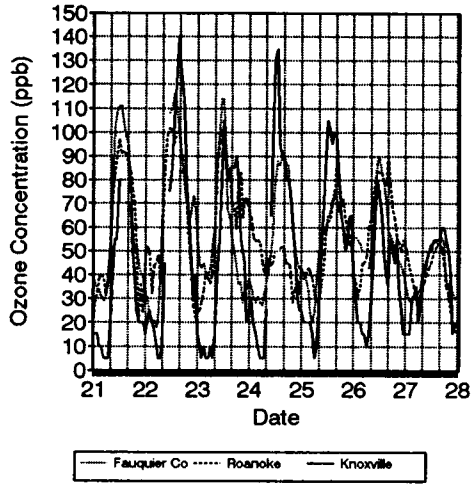
Hourly Ozone Concentrations in East
Tennessee, July 4-11, 1988



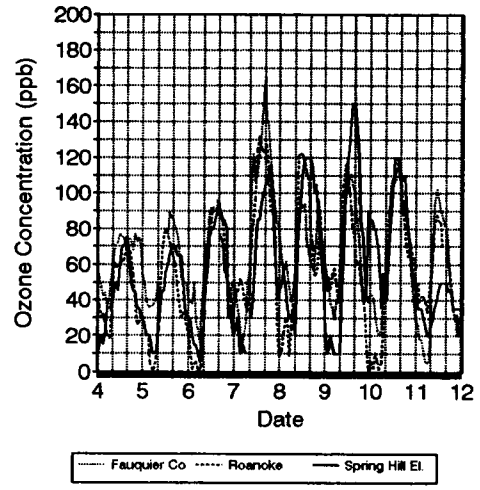
Hourly Ozone Concentrations, Virginia and Knoxville, Tn, June 11-18, 1988



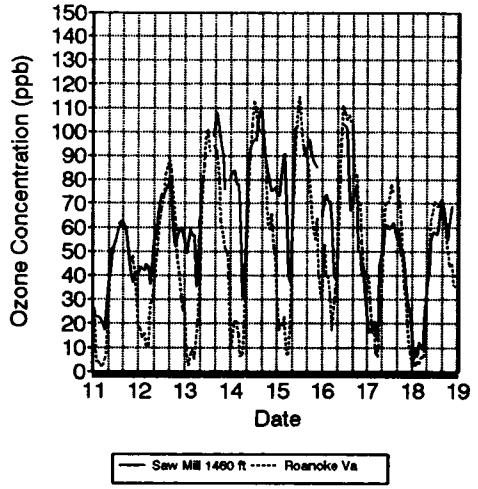
Hourly Ozone Concentrations, Virginia and Knoxville, Tn, June 21-27, 1988



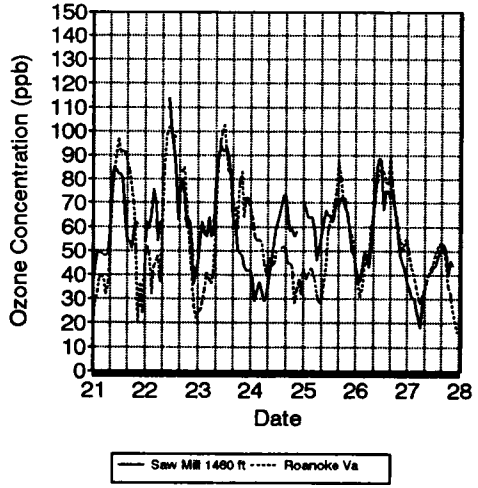
Hourly Ozone Concentrations, Virginia and Knoxville, Tn, July 4-11, 1988



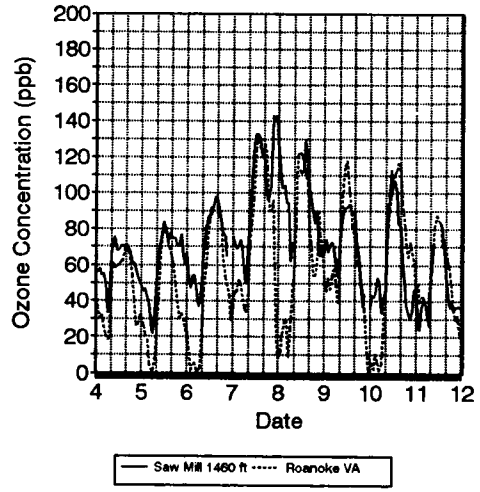
Hourly Ozone Concentrations, Saw Mill Run and Roanoke, Va, June 11-18, 1988



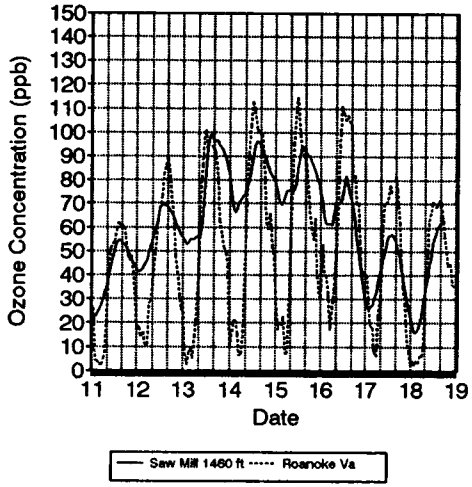
Hourly Ozone Concentrations, Saw Mill Run and Roanoke, Va, June 21-27, 1988



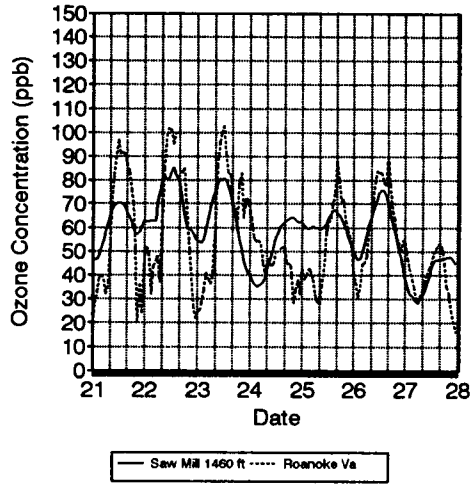
Hourly Ozone Concentrations, Saw Mill Run and Roanoke, Va, July 4-11, 1988



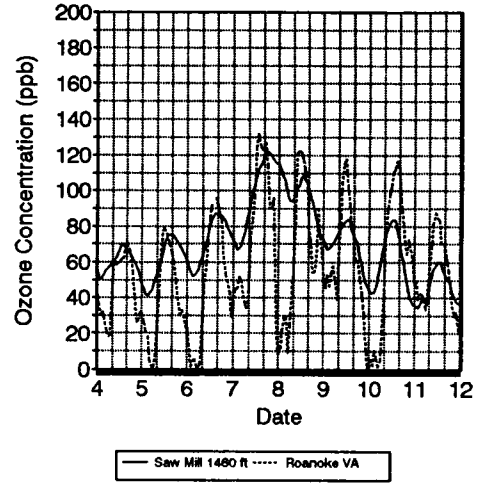
Ozone Aloft With Eleven Hour Dampening, and Roanoke, Va, June 11-18, 1988



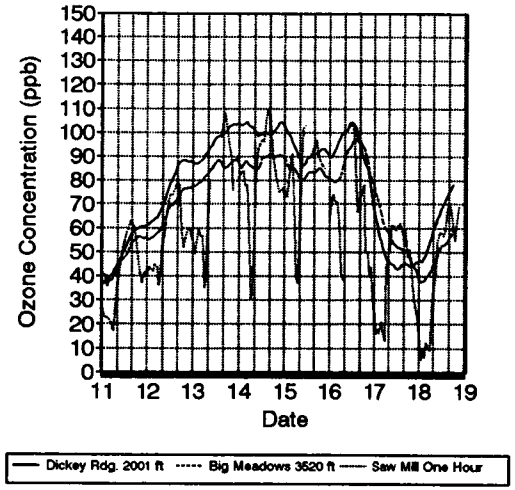
Ozone Aloft With Eleven Hour Dampening, and Roanoke, Va, June 21-27, 1988



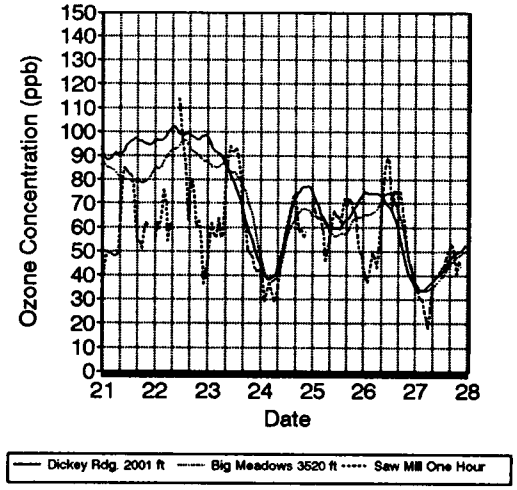
Ozone Aloft With Eleven Hour Dampening, and Roanoke, Va, July 4-11, 1988



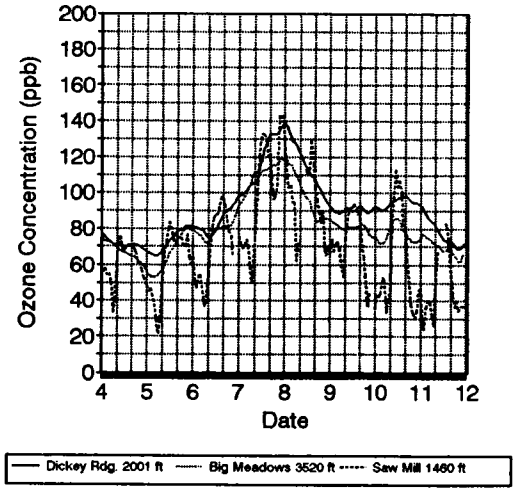
Ozone Aloft With Eleven Hour Dampening, and Saw Mill Run, June 11-18, 1988



Ozone Aloft With Eleven Hour Dampening, and Saw Mill Run, June 21-27, 1988



Ozone Aloft With Eleven Hour Dampening, and Saw Mill Run, July 4-11, 1988



VITA

Eric Kevin Hutton was born in Jefferson City, Tennessee. He graduated from Jefferson County High School in 1985. The following September he enrolled at Virginia Polytechnic Institute and State University (VPI&SU or Virginia Tech). While earning his Bachelors degree, he held several summer jobs as a draftsman and Machine Shop Assistant. In April, 1990, he passed the Engineer in Training Exam. In May, 1990, he received the degree of Bachelor of Science in Electrical Engineering. He also completed minors in Math and Music. The following August he entered the University of Tennessee and became a member of the Air and Waste Management Association. From August, 1990, to December, 1990, he worked with the University of Tennessee's Energy and Environment Resources Center as a Senior Research Assistant, where he assisted with cost analysis of Superfund Sites. From January, 1991, through May, 1993, he worked as a graduate research assistant where he set-up and operated two ozone monitoring stations in the Knoxville area and assisted with the development of inventories of precursors of ozone for Ozone Non-Attainment areas in Tennessee. In December, 1993, he received a Master of Science degree in Environmental Engineering.